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OF THE

# AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED) and Petroleum

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## MILLING METHODS

## 1930

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PAPERS AND DISCUSSIONS PRESENTED AT MEETINGS HELD AT NEW YORK, FEBRUARY, 1928, 1929 AND 1930, AT SAN FRANCISCO, OCTOBER, 1929 AND AT SPOKANE, OCTOBER, 1929

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# FOREWORD

The Milling Committee is charged with the responsibility of securing papers upon the various phases of milling which shall be of timely interest to the members of the Institute. The policy adopted some time ago by the Institute, of publishing special volumes whenever sufficient papers accumulate upon a particular subject to warrant, renders it desirable that the volume cover all of the new developments in the particular field for the period. The difficulty of doing this is apparent when we reflect that all papers are voluntary, there is no remuneration to the author and, despite a good deal of solicitation, committee chairmen are at times disappointed in securing certain papers to round out a subject. It is hoped that the reader will recognize the good points in the present volume and bear with its shortcomings, and, most important, assist in bringing up succeeding volumes to a higher standard of excellence.

GALEN H. CLEVENGER, *Chairman,*
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# Crushing and Grinding, I.—Surface Measurement of Quartz Particles*

By John Gross† and S. R. Zimmerley,‡ Salt Lake City, Utah

(New York Meeting, February, 1928)

A survey of the status of ore dressing in 1923[1] placed particular stress on the need of research in the crushing and grinding of ore, especially on the need for a method of measuring the surface of the products obtained in crushing and grinding and for fundamental data on the law of crushing, in order that intelligent conclusions may be drawn from actual crushing or grinding experiments.

There has been no satisfactory means of determining the surface of crushed products. The results have been judged entirely by the amount of the various sizes produced, based on sieve sizing for particles above 74 microns in size and on microscopic measurement or elutriation for particles below 74 microns, a method which could give only a general idea of what had been accomplished.

The fact that the long controversy between the followers of Kick and of Rittinger has resulted in no accepted conclusion is evidence of the need for fundamental data on the crushing law.

## Some Methods of Measuring Surface of Particles

A dissolution method was used by Wolff to measure surfaces of glass powder. A mixture of sodium carbonate and sodium hydroxide was the solvent and the amount of glass dissolved in two hours from the powder was compared with that dissolved from a glass plate.[2] Lately Herbert F. Kriege has used the dissolution method in determining surface of calcite and limestone.[3]

Dr. Geoffrey Martin and his coworkers in England have also used a dissolution method to determine surface on quartz. They compared the amount of quartz dissolved from the sample in one hour by a hydrofluoric acid solution with the amount dissolved from a measured quartz

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* First in a series of three papers to be published on the subject of Crushing and Grinding.

† Metallurgist, Intermountain Experiment Station, U. S. Bureau of Mines.

‡ Assistant Metallurgist, Intermountain Experiment Station, U. S. Bureau of Mines.

[1] E. A. Hersam: The Status of Research in Ore Dressing. Report to the Milling Committee of A. I. M. E. and U. S. Bureau of Mines (1923).

[2] H. Wolff: Determination of the Surface of Glass Powder. *Ztsch. angew. Chem.* (1922) **35**, 138–140. Abs. in *Chem. Abst.* (1922) **16**, 2017.

[3] Relation between the Fineness of Limestone and Its Rate of Solution. *Rock Products* (July 10, 1926) **24**, 65–68.

cuboid.[4] As Dr. Martin's paper was published shortly after a preliminary publication of the work being done in the Bureau,[5] it would appear that Dr. Martin's investigation and that of the Bureau were carried on at about the same time.

## Work of Bureau of Mines on Surface Measurement of Particles

The Bureau of Mines began work on the problem at the Intermountain Experiment Station, Salt Lake City, in September, 1924. This investigation has been confined to three phases: the development of a method for the measurement of surface of crushed quartz particles; the relation of measured surface of crushed quartz particles to the average diameter as obtained by sieve sizing; and the relation of the work expended in a crushing operation to the surface produced.

This paper deals only with the method of surface measurement of quartz particles. The other phases of the work will be taken up in later papers.

It was realized that no advance in the fundamental investigation of crushing and grinding could be made without a reliable method of surface measurement and that such a measurement would have to be based on some property of the surface of the crushed material. As the surfaces of various minerals have individual physical and chemical properties, it was decided that it was best to begin the investigation on one mineral only. Quartz was selected because the pure mineral could be obtained in quantity and because it has many qualities desirable for the study of crushing. The quartz used was a massive variety obtained in northwestern Utah, having a density of 2.65 and a purity of 99.5 per cent. $SiO_2$.

A number of attempts based on various surface actions such as adsorption and heat of wetting were made to measure surface on quartz particles but all gave unsatisfactory results. After some preliminary work it was decided that a dissolution method based on Wenzel's law—"the reaction velocity between solids and liquids is proportional to the area of contact"[6] —would be the most feasible.

After investigating the solvent power of sodium carbonate, sodium hydroxide and hydrofluoric acid for quartz, hydrofluoric acid was selected as the most suitable solvent and a dissolution method was worked out which gives very reliable results.

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[4] G. Martin, E. A. Bowes, J. W. Christelow: Researches on the Theory of Fine Grinding, Part II. A method of accurately determining experimentally the surface of crushed sand particles. *Trans.* Ceramic Society (1925–26) **25,** 51.

[5] J. Gross, S. R. Zimmerley, S. J. Swainson: Surface Measurement on Finely Ground Particles and Its Relationship to the Crushing Laws. *Bull.* 16, Univ. of Utah (August, 1925), 57–76.

[6] C. W. Ostwald: Theoretical and Applied Colloid Chemistry. Trans. by Martin H. Fisher, 1st ed., New York, 1917. J. Wiley & Sons; S. L. Bigelow: Theoretical and Physical Chemistry. New York, 1920.

During the dissolution of quartz in hydrofluoric acid, the reaction velocity changes, for two reasons: there is a change in concentration of solution, and a change of surface of the solid. In view of these changes, it is clear that the amount of quartz dissolved in a definite period of time is not a true measure of surface. If, however, the reaction velocity or rate of dissolution for various periods of time is plotted, a curve is obtained, which, if extrapolated to the zero time ordinate, will give the rate of dissolution before any change of surface or any change in the solvent has taken place, and which is a true index of surface. This rate of dissolution, expressed in percentage of the original sample at the zero time ordinate, is designated herein as the "Initial Rate" or simply "I. R."

## The Dissolution Method

Improvements were made in the procedure, which gave increased accuracy. Details of the present procedure follow:

*Preparation of Sample.*—The quartz is cleaned by removing the bulk of the abraded iron with a magnet and any remaining iron or other impurity with hot nitric and hydrochloric acid. It is then thoroughly washed and dried.

*Weight of Sample.*—The amount of sample taken for dissolution depends largely on the size of the particles. The sample should preferably be large enough so that 50 mg. of silica is dissolved in 1 hr. On the other hand, the sample should not be so large that the concentration of the solution is unduly lowered. With fine material a 1-gram sample may be satisfactory while with coarser material a 16-g. sample may be advisable. In routine work, seven samples of equal weight are taken, six for dissolution tests and one for ignition loss.

*Apparatus.*—The dissolution tests are made in tubes 6.5 in. long, of various diameters, dependent on the volume of solvent. The tubes finally used, which are entirely satisfactory as to acid and abrasion resistance, are made of one of the Bakelite products known as Dilecto XX. Corks are used to close both ends of the tubes. Agitation is accomplished by rotating the tubes end for end at 20 r.p.m. in a thermostatically controlled water bath capable of holding six 25 c.c. tubes.

*Standard Solution.*—The standard hydrofluoric acid solution is prepared from C. P. hydrofluoric and carefully standardized against a fresh standard solution of sodium hydroxide, which has previously been standardized by means of benzoic acid. The standard concentration of solution used in these tests is 3.66 normal, or 73.2 g. HF per liter. This concentration has been adhered to because it was found satisfactory in some preliminary work. A standard of 60 to 80 g. per liter would have been just as satisfactory. The volume of solution used varies from 25 to 250 c.c. The 25 c.c. volume allows ease of manipulation and rapidity of filtering and therefore is usually used.

*Dissolution of the Quartz.*—The tubes containing the hydrofluoric acid are rotated in the water bath for one-half hour to attain constant temperature. The tube is removed, the quartz sample quickly dropped in, and the tube replaced in the water bath, which is held to within 0.1° of 25° C., and agitated for the desired length of time. The tube is then removed, the contents rapidly filtered by vacuum and thoroughly washed. The contact period is taken from the time the quartz is dropped into the tube to the time when the wash water is applied. The filter paper with the quartz is placed in a weighed platinum crucible and slowly heated in a muffle furnace. When the filter paper has ceased burning, the cover is removed and heating is continued until no carbon from the filter paper remains. The crucible and contents are placed in a dessicator to cool, then are weighed.

*Time Periods of Dissolution.*—Short periods of time for the dissolution tests are desirable in giving points close to the zero time ordinate; on the other hand, the data obtained for short periods of time are more liable to error than with longer periods. From the results of many tests, it was decided that the ½-hr. period is the shortest from which reliable data are obtainable. In all the later work dissolutions were made for ½-hr., 1-hr., 1½-hr., and 2-hr. periods, the ½-hr. and the 1-hr. dissolutions being duplicated.

*Ignition Loss.*—The loss in weight of the quartz as determined by the dissolution test must be corrected for "ignition loss." This is a small value, usually about 0.1 per cent. and fairly constant, probably due to moisture and residual carbon from abraded iron. A sample of the quartz equal in weight to that of the samples for dissolution is placed in a filter paper, washed, ignited in a weighed platinum crucible, cooled and weighed. This ignition loss is deducted from the loss in weight as determined by the dissolution test to obtain the true weight of silica dissolved. Some experiments were made in which the quartz was heated before the dissolution tests. It was thought that this might obviate the need for an ignition correction. The results were erratic, possibly due to some disintegration of the quartz.

*Care in Manipulation.*—Extreme care in manipulation is necessary to avoid loss of quartz particles. This is especially true when handling fine material and with the short-time-period dissolutions.

## Determining the Initial Rate (I. R.)

From the experimental data two curves are drawn, the cumulative curve and the rate curve, as follows:

*a.* The cumulative curve is per cent. silica dissolved plotted against time (curves $C$ and $C^1$ in Fig. 1). This curve must pass through the origin.

*b.* The rate curve is per cent. silica dissolved per hr., plotted against time (curves $R$ and $R^1$ in Fig. 1). This curve is really a per cent. rate

curve but is designated as the "rate curve" for simplicity. The extrapolation of the rate curve to the zero time ordinate gives the initial rate, or the index of surface.

Both curves must be smooth if the data are correct. Any doubtful points are checked by repeating. The reliability of the method depends largely on the accuracy with which the extrapolation for the I. R. is made. During the earlier part of the work the rate curves were extrapolated graphically. This was not entirely satisfactory and it was realized that a mathematical extrapolation was highly desirable.

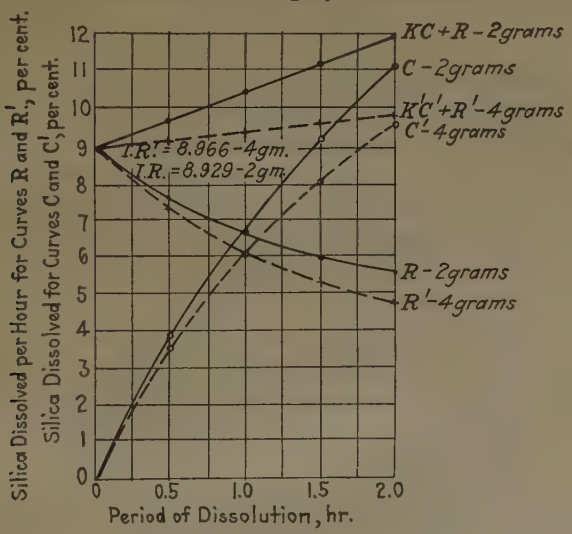


FIG. 1.—EXTRAPOLATION OF THE I. R. VALUES ON A CRUSHED QUARTZ SAMPLE.

The slope of the tangent to the cumulative curve at any point on the curve represents the rate at that time; likewise the slope at the origin represents the instantaneous rate at zero, or the initial rate. Many attempts were made to fit standard curves to the data and to obtain the I. R. value from the tangent at the origin of such a curve, but all were unsatisfactory. Expressions, however, were finally derived for both curves which fit the experimental data. These expressions are:

$$R = \frac{A + at}{1 + Kt} \tag{1}$$

$$C = \frac{At + at^2}{1 + Kt} \tag{2}$$

in which $R$ = per cent. silica dissolved per hour.
$C$ = per cent. silica dissolved.
$A$ = initial rate.
$a$ = constant.
$k$ = constant.
$t$ = time in hours.

The derivation of these expressions may be seen by referring to Fig. 2, in which $KC + R$ is a straight line. This line, together with $A$ and $R$, intersects the zero time ordinate at the Initial Rate. From this it will be noted that by the combination of the curves $C$ and $R$ the value of I. R. is really obtained by the extrapolation of a *straight line*, a far more reliable procedure than the extrapolation of the rate curve only. $A$ is also the point where the tangent of the cumulative curve at zero cuts the 1-hr. ordinate.

The general equation in which $KC + R$ equals a straight line is:

$$KC + R = A + at \tag{3}$$

in which $at$ equals the distance from $A$ to the straight line.

In equation (3) there are three unknown values, $K$, $A$, and $a$. Taking the values for $R$ and $C$ for the ½, 1 and 1½-hr. periods, $A$ (initial rate) is calculated. The value for the 2-hr. period is then calculated by means of equation (1) or (2) and checked against the

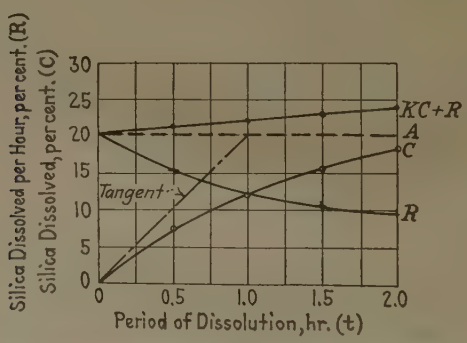


FIG. 2.—GRAPH FOR THE MATHEMATICAL EXPRESSION OF THE CURVES $C$ AND $R$.

experimental value. While the experimental data may vary from the exact time periods by a small amount, this is corrected to the exact time periods either by interpolation on the smooth curves $R$ and $C$ or by interpolation from a "difference in rate" curve. Exact time periods are used in the calculations for convenience.

Having established the equation for the cumulative curve, values may be accurately calculated for any point on the curve as close to zero as may be desirable. If the slope of the secants between such points and zero be plotted against the time value for the points, the resulting curve extrapolated to zero time will give the limit of the slopes of the secant,

which will be the slope of the tangent. The slope of the tangent of the cumulative curve at zero is, of course, the rate at the beginning of the reaction. Such a procedure is the same as the plotting of the rate curve, and the I. R. of the rate curve is the same value as the slope of the tangent at zero on the cumulative curve.

These expressions for the curves are acceptable from the fact that the calculated curves check the experimental data in all cases, even for dissolution periods up to 10 hr., the maximum time to which dissolution tests have been carried.

In the extrapolation for the I. R., the nature of the rate curve has considerable influence on the accuracy of the extrapolation.

The most desirable curve is one approaching a straight line parallel to the time axis; that is, one with zero slope. This curve can be extrapolated with the greatest accuracy. Increased curvature and increased slope of the rate curve diminish the accuracy of the extrapolation.

The conditions that give increased curvature are: greater surface on the sample; a smaller ratio of solvent to solid; and a lower concentration of the solvent. The conditions that give increased slope are: greater surface on the sample; a smaller ratio of solvent to solid; and higher concentration of the solvent. A greater curvature is more serious than a greater slope. With quartz having a small surface, a flat curve is obtained that is easily extrapolated, but with fine material, having a large surface, the conditions that increase accuracy are, primarily, a large ratio of solvent to solid and, secondarily, a high concentration of solution. An increased ratio of solvent to solid is accompanied by increased difficulties in manipulation and the selected ratio of solid to solvent is therefore largely a matter of judgment. The use of a solvent of other than standard concentration is not desirable except in extreme cases, as the I. R. values vary with varying concentrations.

As the rate curve is a percentage rate curve, and as the percentage rate of dissolution at the start is the same irrespective of the ratio of solvent to solid, it follows that if two series of dissolution tests are made using two different ratios, two rate curves will be obtained which should extrapolate to the same I. R. point. This gives a valuable means for checking the correctness of the data.

An example of the data secured on 2 and 4-g. samples of crushed quartz, using the same volume of solvent, is given in Table 1.

The experimental data are plotted as cumulative curves ($C$ and $C'$) and as rate curves ($R$ and $R'$) in Fig. 1. From these smoothly drawn curves the accuracy of the data is judged. By the use of the mathematical expression given previously, the various values for $KC + R$ and $K'C' + R'$ are obtained, which give the straight lines intersecting the zero-time ordinate at $A$, the I. R. point.

### *Dissolution of Different Quartz Samples*

It is well known that the rate of dissolution of quartz varies with the direction of the crystal axes. Some work done on the dissolution of quartz crystals indicates that the dissolution in the interior of the crystal proceeds in the direction of the vertical axis. If dissolution proceeds along a certain axis in a crushed quartz particle, it may be assumed that this effect will be compensated in all cases because of the large number of particles used in the determination.

TABLE 1.—*Data on Dissolution Tests—Crushed Quartz*

| 2-gram Sample | | | | | 4-gram Sample | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Period of Dissolution, Hr. | Silica Dissolved | | | | Period of Dissolution, Hr. | Silica Dissolved | | | |
| | Weight, Mg. | $C$ Value, Per Cent. | $R$ Value, Rate, Per Cent. per Hr. | | | Weight, Mg. | $C'$ Value, Per Cent. | $R'$ Value, Rate, Per Cent. per Hr. | |
| *Experimental data* | | | | | | | | | |
| 0.500 | 75.2 | 3.760 | 7.520 | | 0.508 | 146.4 | 3.658 | 7.200 | |
| 1.000 | 132.5 | 6.625 | 6.625 | | 1.000 | 243.4 | 6.085 | 6.085 | |
| 1.514 | 181.3 | 9.073 | 5.993 | | 1.500 | 317.3 | 7.932 | 5.288 | |
| 2.000 | 221.7 | 11.086 | 5.543 | | 2.004 | 381.1 | 9.527 | 4.754 | |
| *Calculated data* | | | | | | | | | |
| | | | | $KC + R$ | | | | | $K'C' + R'$ |
| 0.500 | | 3.760 | 7.520 | 9.678 | 0.500 | | 3.610 | 7.220 | 9.162 |
| 1.000 | | 6.625 | 6.625 | 10.428 | 0.508 | | 3.658 | 7.200 | 9.168 |
| 1.500 | | 9.009 | 6.006 | 11.177 | 1.000 | | 6.085 | 6.085 | 9.359 |
| 1.514 | | 9.072 | 5.992 | 11.199 | 1.500 | | 7.932 | 5.288 | 9.555 |
| 2.000 | | 11.106 | 5.553 | 11.928 | 2.004 | | 9.407 | 4.694 | 9.755 |

Error in 2 hr. pt. = −0.18 per cent.
I. R. = 8.929
$a$ = 1.499
$K$ = 0.574

Error in 2 hr. pt. = +1.28 per cent.
I. R.′ = 8.966
$a'$ = 0.393
$K'$ = 0.538

Average I. R. = 8.948
Error from average I. R. = 0.21 per cent.

To see whether any marked difference existed in the dissolution rate of different samples of quartz, three samples, all having the same density, were prepared.

Sample 1.—Massive quartz of −100 + 150 mesh, as used in the regular work.

Sample 2.—Ottawa (Utica Brand) sand, + 28 mesh, after cleaning, was crushed to pass a 65-mesh sieve, and from this a −100 + 150 mesh product was prepared.

Sample 3.—A large quartz crystal was crushed to pass a 65-mesh sieve and from this a − 100 + 150-mesh product was prepared.

These three samples presumably consisted of similar particles, and so appeared under the microscope.

Dissolution tests were made on the three samples, using 2-g. charges with 25 c. c. of standard hydrofluoric solution. The results of these tests are given in Tables 2, 3 and 4, the Initial Rates obtained being as follows:

| | Initial Rate | Variation from Average |
|---|---|---|
| Massive regular crushed quartz | 2.489 | −1.4 |
| Ottawa (Utica) sand, crushed | 2.566 | +1.6 |
| Crystal, crushed | 2.518 | −0.2 |
| Average | 2.524 | |

These data show that whatever effect the direction of dissolution in the crystal quartz may have on the rate, the same effect occurs in massive quartz. In other words, if the dissolution proceeds only in the direction of the vertical axis in a quartz crystal, the dissolution in other quartz is the same. Crushed quartz, therefore, has a definite rate of dissolution in spite of the fact that dissolution does not proceed equally in all directions.

Table 2.—*Data on Dissolution Test Crushed Quartz* 100/150 *Mesh*

2-gram Sample

| Period of Dissolution, Hr. | Silica dissolved | | | |
|---|---|---|---|---|
| | Mg. | *C* Value, Per Cent. | *R* Value, Rate, Per Cent. per Hr. | |
| | | *Experimental data* | | |
| 1.00 | 46.0 | 2.300 | 2.300 | |
| 1.00 | 45.4 | 2.270 | 2.270 | |
| 3.00 | 122.8 | 6.140 | 2.047 | |
| 6.00 | 209.2 | 10.460 | 1.743 | |
| 8.83 | 284.4 | 14.220 | 1.610 | |
| | | *Calculated data* | | |
| | | | | $KC + R$ |
| 1.00 | | 2.290 | 2.290 | 2.613 |
| 3.00 | | 6.045 | 2.015 | 2.867 |
| 6.00 | | 10.560 | 1.760 | 3.249 |
| 8.83 | | 14.199 | 1.608 | 3.609 |

I. R. = 2.486
$a$ = 0.127
$K$ = 0.141

TABLE 3.—*Data on Dissolution Test Ottawa (Utica) Sand Crushed to 100/150 Mesh*

2-gram Samples

| Period of Dissolution, Hr. | Silica Dissolved | | | |
|---|---|---|---|---|
| | Mg. | *C* Value, Per Cent. | *R* Value, Rate, Per Cent. per Hr. | |
| | | *Experimental data* | | |
| 1.16 | 55.8 | 2.790 | 2.405 | |
| 2.00 | 92.0 | 4.600 | 2.300 | |
| 3.06 | 134.2 | 6.710 | 2.193 | |
| 4.02 | 169.8 | 8.490 | 2.112 | |
| | | *Calculated data* | | |
| | | | | $KC + R$ |
| 1.00 | | 2.420 | 2.420 | 2.686 |
| 1.16 | | 2.783 | 2.399 | 2.705 |
| 2.00 | | 4.600 | 2.300 | 2.806 |
| 3.06 | | 6.717 | 2.195 | 2.934 |
| 4.00 | | 8.460 | 2.115 | 3.046 |
| 4.02 | | 8.498 | 2.114 | 3.049 |

I. R. = 2.566
$a$ = 0.120
$K$ = 0.110

TABLE 4.—*Data on Dissolution Test Quartz Crystal Crushed to 100/150 Mesh*

2-gram Sample

| Period of Dissolution, Hr. | Silica Dissolved | | | |
|---|---|---|---|---|
| | Mg. | *C* Value, Per Cent. | *R* Value, Rate, Per Cent. per Hr. | |
| | | *Experimental data* | | |
| 0.99 | 45.9 | 2.295 | 2.318 | |
| 1.01 | 45.3 | 2.265 | 2.243 | |
| 2.01 | 86.2 | 4.310 | 2.144 | |
| 3.03 | 124.7 | 6.235 | 2.058 | |
| 3.98 | 160.3 | 8.015 | 2.014 | |
| 4.00 | 159.0 | 7.950 | 1.988 | |

TABLE 4.—(*Continued*)

| Period of Dissolution, Hr. | Silica Dissolved | | | |
|---|---|---|---|---|
| | Mg. | *C* Value, Per Cent. | *R* Value, Rate, Per Cent. per Hr. | |
| | *Calculated data* | | | |
| | | | | $KC + R$ |
| 0.99 | | 2.260 | 2.283 | 3.155 |
| 1.00 | | 2.280 | 2.280 | 3.160 |
| 1.01 | | 2.302 | 2.279 | 3.088 |
| 2.00 | | 4.292 | 2.146 | 3.803 |
| 2.01 | | 4.311 | 2.145 | 3.809 |
| 3.03 | | 6.236 | 2.058 | 4.465 |
| 3.98 | | 7.968 | 2.002 | 5.078 |
| 4.00 | | 8.000 | 2.000 | 5.088 |

I. R. = 2.518. $a = 0.643$. $K = 0.386$.

## ACCURACY OF THE DISSOLUTION METHOD

There are a number of factors that enter into the accuracy of the determination of the I. R. value. Their probable effect on that accuracy is considered in the following paragraphs.

*The Sample.*—The accuracy with which the sample represents the material increases as the material becomes finer, the larger number of particles giving a more representative sample. The variation in two samples of equal weight is compensated by taking the average results of two dissolutions. This is especially advisable in the short-time-period dissolution. When a product contains coarse as well as fine material, it is practically impossible to weigh directly a number of samples having even approximately equal amount of surface. Obviously, in this case serious errors are likely. If such a product is separated into two or more sizes by sieving and a composite sample made by weighing out each size in proportion to the weight it represented in the original material, representative samples will be obtained for the dissolution. An error may result from inaccurate weighing, but a large error of that kind is at once detected in the data and small inaccuracies are compensating and well within 0.2 per cent.

*Manipulation.*—Loss in handling may be the cause of erroneous results especially with very fine material. Experiments made on loss in handling −200-mesh material indicate that with reasonable care such a loss represents a maximum error of less than 2.0 per cent. As similar losses may occur in the determination of the ignition correction, this tends to compensate such errors. A slight error in the time of the test may occur, but as the time can be observed accurately to within 10 sec., the maximum error from this cause would be 0.6 per cent. This again is a compensating error.

*Agitation.*—If the rate of diffusion is slow compared to the rate of dissolution, it is clearly evident that the amount of agitation, or the rate of settling of the particles, would have a decided effect on the amount of solid dissolved. If, however, the rate of dissolution is slow compared to the rate of diffusion, little or no effect will be noticed on account of the movement of the solid particles in the solvent. Such cases are known to exist.[7] The dissolution of quartz in hydrofluoric acid seems to belong to this class as the effect of increased agitation or movement of the particles through the solution has been found experimentally to have such a small effect that it is negligible as a source of error. Sufficient agitation is given to prevent the quartz from packing in the end of the tube and thus possibly lessening the action due to masked surfaces.

*Abrasion.*—If abrasion of the particles takes place during dissolution, a greater amount of silica will dissolve as more surface is exposed to the solvent. This may occur with easily abraded minerals, but quartz is not abraded by the agitation during a dissolution test. Samples of quartz were agitated with distilled water for 4 hr. in the same manner as were the dissolution tests. After drying, the quartz gave the same dissolution rate as like samples which had not been given a preliminary agitation.

*Temperature.*—The temperature is controlled within 0.1° C. Tests made at 20°, 25° and 30° C. on several samples of quartz showed that, with a temperature variation of 0.1° C., the error in the I. R. determination is less than 0.5 per cent., a compensating error.

*Concentration of Solution.*—Tests made with standard strength, half strength and double strength hydrofluoric acid showed that a variation of 0.25 per cent., the limit of accuracy in standardizing the hydrofluoric, caused an error of less than 0.4 per cent. in the I. R. determination.

*Ignition Correction.*—The ignition correction is small and many repeat ignitions checked well within 0.5 mg. An error of 0.5 mg. causes an error of 2.5 per cent. in the initial rate when 50 mg. of quartz is dissolved in ½ hr. With larger amounts dissolved, the error in the I. R. decreases.

*Reproducibility of Results.*—As most of the possible sources of error are compensating, an average value of two duplicate dissolutions should give a fairly accurate figure. The results from several hundred duplicate dissolutions showed that the probable variation is less than 1.0 per cent. from the average.

*Effect of Error on the I. R. Value.*—An error in any of the dissolutions has more effect on the Initial Rate when the rate curve has a great curvature. In rate curves as ordinarily obtained, an error of 1 per cent. in the ½-hr. and 1-hr. points affects the I. R. by about 6 per cent., and

[7] E. K. Rideal: An Introduction to Surface Chemistry, 193. Cambridge Univ. Press, 1926.

F. C. Huber and E. Reid: Influence of Rate of Stirring on Reaction Velocity. *Ind. & Eng. Chem.* (1926) **18**, 535.

the same error in the 1½-hr. and 2-hr. points affects the I. R. by about 2.5 per cent. If the curvature of the rate curve is not great, an error of 1 per cent. in any of the dissolutions becomes glaringly apparent. If the I. R. is calculated from the ½-hr., 1-hr., and 1½-hr. points, and if from this calculation the 2-hr. point checks within 2 per cent. of the calculated 2-hr. point, it indicates that the I. R. is not off more than 4 per cent., unless the rate curve has an unusual curvature due to a low ratio of solution to solid.

*Probable Accuracy of the I. R. Value.*—As the errors in determining the points for the rate curve are largely compensating, and as comparatively small errors are readily detected if a ratio of solution to solid is chosen so that the curvature of the rate curve is not too great, it is thought that, with careful manipulation in the dissolution tests, the determination of the I. R. is within 5 per cent. of the correct value. This conclusion is more than verified in the results from 21 I. R. determinations in which two different ratios of solvent to solid were used as a check. These tests were made on a variety of samples, sized and unsized, with I. R. values ranging from 0.816 to 128.703. The average I. R. variation of these tests was 0.77 per cent. from the average, the greatest variation being 2.69 per cent. from the average.

*Effect of Fine Particles on the Dissolution Rate.*—In the dissolution of quartz with the standard hydrofluoric acid, a layer 0.25 micron thick is dissolved in 1 hr. Therefore particles of a diameter of 0.5 micron or less dissolve entirely in this period of time. It may be assumed, however, with a fair degree of assurance, that there is a regular gradation of the small sizes in an ordinarily crushed or ground product; that the complete dissolution of particles is a gradual process, and is therefore taken into account in the extrapolation of the rate curve to the zero time ordinate. If, however, material consisting entirely of particles of 0.5 micron or less is to be subjected to measurement of surface, a solvent of much lower concentration must be employed. That the ultimate solubility increases with the fineness of the substance does not affect the I. R. value, as this is a measure of rate; and if Wenzel's law holds, the rate of dissolution is a measure of the surface exposed to the solvent irrespective of the ultimate solubility. The reliability of the dissolution method for surface determinations on quartz will be considered further in a subsequent paper on crushing and grinding, in connection with the relation of measured surface to average size of particles.

## *Calibration of the I. R. Value*

The surface measurement figure obtained and expressed by the I. R. value is a relative value only but may be directly compared with any other I. R. value on the same class of material when the dissolution tests

have been made with the same concentration of solution and at the same temperature.

It is highly desirable, however, not only for convenience but for comparison with other materials, that the actual surface of the quartz be known. Attempts were made to calibrate the I. R. value by subjecting thin polished plates of quartz to the dissolution method. This failed because the polished surfaces rapidly became pitted.

Another attempt was made to calibrate the I. R. value by subjecting quartz crystals of known surface to the dissolution method. In a quartz crystal the dissolution proceeds from the three alternate intersections of the rhombohedral faces at each pyramid, the prism being untouched. As these lines represent no surface at the beginning of the dissolution, the rate curve obtained has a curvature opposite from that obtained on quartz particles and actually gives an I. R. value of zero.

As both the thin polished plates and the quartz crystals were found unsuited for calibration purposes, recourse was had to another method. Quartz readily takes on a strongly adherent coating of silver when placed in a modified mirroring solution. The thickness of this coating varies, however, with strength of solution, with time, with temperature, with agitation, with amount of surface in contact with the solution, and with other conditions.

As the control of a definite layer of silver on quartz depends on so many conditions, it was impossible to reproduce results in two consecutive experiments. When, however, two different samples of quartz are given similar contact with the same solution, it is reasonable to believe that the layer produced on all of the material will be of equal thickness. Experiments indicated that quartz crystals, quartz particles and glass take on a layer of equal thickness when given similar agitation in the same solution.

Ottawa sand (the I. R. value of which had been determined) was chosen as the material to compare with 15 quartz crystals, the surface of which had been determined as 6.60 sq. cm., by the camera lucida. Ottawa sand was chosen for this purpose because the surface of this material is much nearer that of theoretical spheres than is crushed quartz, and also because it is practically free from cracks which affect the dissolution rate.[8] The quartz crystals and sized Ottawa sand were placed in a tube with the silvering solution, constant movement of the quartz being obtained by reversing the tube vertically so that the quartz was continuously falling from end to end. After 30 min. the coated quartz was thoroughly washed, dried and weighed. The silver on the crystals was determined by weight and the silver on the Ottawa sand was dissolved and determined by titration.

[8] The effect of cracks on the dissolution rate will be discussed in a subsequent paper in connection with their significance on surface measurements of crushed quartz.

The results given in Table 5 are the averages of eight or more experiments for each size of Ottawa sand. A certain effect was found to be due to the settling rate of the particles and a correction was applied to compensate this.

TABLE 5.—*Surface Measurements of Ottawa Sand by Silver Coating*

| Sieve Size | Surface as Determined by Silver Coating, Sq. Cm. per Gram | Theoretical Surface Cubes or Spheres, Sq. Cm. per Gram | Ratio of Measured to Theoretical Surface | Initial Rate I. R. | Factor to Convert I. R. to Sq. Cm. per Gram |
|---|---|---|---|---|---|
| 28/35 | 60.97 | 45 | 1.355 | 0.358 | 170.3 |
| 35/48 | 83.64 | 63.5 | 1.317 | 0.497 | 168.3 |
| 48/65 | 118.23 | 90 | 1.314 | 0.732 | 161.5 |
| 65/100 | 176.40 | 127 | 1.389 | 1.020 | 172.9 |
| 100/150 | 249.95 | 180 | 1.389 | 1.389 | 180.3 |
| 150/200 | 338.72 | 254 | 1.334 | 1.923 | 176.1 |

No great degree of accuracy is claimed for the silver-coating method nor is accuracy necessary. The initial rate figures accurately express surface and therefore give true comparisons of surface. The conversion of the I. R. to a definite measure is a convenience only.

The calibration figure has been taken as 170, the factor by which the I. R. value is multiplied to give square centimeters per gram. As no other method of calibration was available, the results obtained by the silver-coating method must be accepted until some other method of calibration is found to be more accurate.

### *Utilization of the Dissolution Method*

The dissolution method for the measurement of surface on quartz has been used in a study of surface measurements on sized quartz, which will be presented in the second paper on Crushing and Grinding. The method has also been used in determining the surface produced in a crushing operation, the results of which will be given in the third paper on Crushing and Grinding.

It is hoped that later a series of grinding experiments may be undertaken, using quartz, in which a comparison between surface produced and work input may be obtained for various machines or for the same machine under various conditions. Such experiments will necessarily have to be confined to material of which the surface may be measured. The possibility of being able to measure surface on ore seems remote. It was thought at one time that it might be possible to coat ore with some substance, and then subject the coating to the dissolution method. Some experiments along this line were tried with silver-coated quartz but were not promising.

A study of surface measurement of calcite is now being made and it is hoped that pyrite and galena may ultimately be included in the investigation. This would give comparable results on two sulfides, one with and one without cleavage, and two gangue minerals, one with and one without cleavage.

## Summary

A method for surface measurement of quartz has been developed which depends on its rate of dissolution in hydrofluoric acid.

The various conditions affecting the accuracy of the test have been investigated, the conclusion being that the dissolution method gives results of surface measurement of quartz within 5 per cent. of the true value.

By comparing the surface measurement of similarly sized products from three different quartzes, it is concluded that the dissolution rate of all ordinary quartz is the same.

It is shown that the rate of dissolution of quartz crystals is not a measure of surface, as the rate of dissolution is not equal in all directions.

A calibration figure has been obtained by silver-coating quartz, from which the relative surface figure obtained by the dissolution method may be converted to specific surface.

## Acknowledgments

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## DISCUSSION

A. F. Taggart, New York, N. Y. (written discussion).—The authors of this paper are to be commended for a large amount of ingenious and painstaking work directed toward the first step of the answer to that difficult question: "What is the work of crushing?" It has been apparent for years that the usual methods of sizing analysis were inaccurate in the coarser sizes and completely inadequate in the finer; and that, if the measure of useful work done in crushing is change in size, the first essential in quantification is an accurate method of size determination. If Rittingers' theorem that the useful work done is proportional to the new surface produced should ultimately be found to hold, a measurement of surface will be necessary and sufficient; if, on the other hand, Kick's theorem that the useful work done is proportional to the reduction in average particle volume is correct, it will be necessary either to extend surface-measurement methods to cover translation from total surface to average volume, or else to devise direct means to measure this latter quantity.

The present research has utility in other fields. Probably a majority of the uses of fine powders depend on surface action, the rapidity and extent of which is, naturally some function of the total surface area of the powder. Present methods of determina-

tion of this quantity almost invariably depend on calculation based on an approximation of average grain diameter, and cursory examination of the methods of such approximation and calculation is sufficient to expose the inadequacy of the methods. If suitable solvents can be found for such powders, a method of the general nature described in the present paper should have considerable application.

The weak point in the new method, as the authors point out, is in the extrapolation to zero time in order to determine initial rate of solution (I. R.), which is taken in a comparative index of surface. All extrapolation is dangerous and this is particularly true when it involves, as it does the present case, passage from experimental values of relatively great magnitude through a zone in which such experimental values as exist are confessedly nonconcordant to the point—zero time—near which experience teaches us to expect markedly greater activity than at any other point in the range. The assumption on which this extrapolation is justified, made on page 19, "that there is a regular gradation of the small sizes in an ordinarily crushed or ground product" and "that the complete dissolution of particles is a gradual process," is questionable. Microscopic study of fine quartz suspensions in Columbia University laboratory indicates that there is a rather definite minimum size of particle in a suspension of ground quartz in distilled water. The absence of particles near the limit of visibility in a high-power microscope with dark-field illumination may be due to solvation of the originally small particles or to an initial absence; probably it is due in part to both causes. If the assumption is made that there is no limiting lower size, it must be assumed that subdivision proceeds to molecular dimensions, in which case the surface of the very fine material would be disproportionately great, and the initial solution rate would be in even greater disproportion for the reason that solution of these very fine particles is not so greatly slowed down by a concentrated film of reaction products surrounding it as is the solution of coarser particles. If, on the other hand, the absence of sizes down to the limit of microscopic visibility means solvation of the small particles, their rate of reaction with hydrofluoric acid should be relatively very great, and such a disproportionate rate would vitiate the assumption of gradual solution and, therefore, the extrapolation to zero.

The transformation from relative surface index to specific surface areas, attempted on pages 19 to 21, is not convincing. It is hard to see why fragments of crystalline quartz are not susceptible to all of the irregularities of solution rate exhibited by an individual quartz crystal; in fact, the pitting of the quartz plate, which means, of course, an uneven rate of solution at different points, would seem to be conclusive evidence that fragments, like crystals, corrode irregularly. If this is so, then the dissolution measurements can never be more than comparative.

The reasoning with respect to the silver coatings also seems to present some discrepancies. Thus, if the thickness of silver coating depends, among other things, on the "amount of surface in contact with the solution" and "it was impossible to reproduce results in two consecutive experiments," it does not seem "reasonable to believe that the layer produced on all of the material will be of equal thickness" when "two different samples of quartz are given similar contact with the same solution," since the two different samples must, if different, present different amounts of surface to the solution. The statement: "Experiments indicated that quartz crystals, quartz particles and glass take on a layer of equal thickness when given similar agitation in the same solution" would, if the experimental data were conclusive, negative the original statement that the deposition varies with the amount of surface in contact with the solution.

The results in Table 5 are extremely interesting. It is to be hoped that the authors will supplement their paper by giving the detailed results for the eight or more experiments averaged to determine the figures of the table, in order that the adequacy of the averages may be apparent.

In view of the authors' own characterization of the silver-coating method on page 21 and of the apparent discrepancies in the reasoning thereon, it would seem safer not to accept the dissolution method as one capable of application in determining specific surface, but to restrict it to comparative measurements. It would also seem safer to restrict the data upon which statements of comparative surface are to be based to the region in which concordant experimental results are obtainable. Thus restricted the method outlined should give figures that will permit investigation of the truth of Rittinger's thereom and, if it is found to hold, will permit comparisons of crushing operations to be made on the basis of the new surface produced.

C. E. Locke, Cambridge, Mass.—I feel that in this extrapolation to the initial rate the authors have seized upon the best possible process available, and I have not felt that there was great possibility of error in so doing. Professor Taggart, have you any definite evidence of the quartz in the distilled water?

A. F. Taggart.—Nothing but that already given.

C. E. Locke.—Did not Gaudin in his work get certain evidence that there were particles even down to molecular size in crushed rock?

A. F. Taggart.—I do not think the evidence was conclusive.

C. E. Locke.—I was under the impression he at least spoke of it in his paper, because you will recall that he likewise attacked the problem of the Rittinger theory, and worked out some results. My impression was that he made an assumption that these particles did go 'way down to the molecular size.

It seemed to me in connection with this paper that the authors have made an admirable start and have reported the first step in the investigation which we hope will solve the long controversy over the Rittinger-Kick theories and laws.

I would like to ask the authors why they did not preheat the quartz as well as the solution. They carefully preheated the solution but poured the crushed quartz into the solution. There was an opportunity to avoid any error due to the cool quartz by simply heating the quartz in the same way they heated the solution.

I want to congratulate the authors on the work; it represents, of course, only a small amount of the actual experimental data that they must obtain, and I believe they are working along the right line to give us something that is well worth while.

G. L. Oldright, Salt Lake City, Utah.—The authors have carried out this work to a high degree of accuracy; that is, in terms of ordinary engineering experiments. When they say the results were not concordant, they mean that they were not inside the percentage of error set for themselves as shown in the paper.

As far as extrapolation is concerned, they performed many experiments with varying periods of time, to verify the mathematical formula for rates of solution, which could be used to predict what other rates of solution they were going to get and how much would be dissolved. They felt sure of their results.

The reason, of course, for extrapolation to the initial rate is that the surface is diminished as you go on, and if you do not go back to it you do not know what the original surface was.

They bring up an interesting point in regard to dissolving crystals. One would think that in measuring the rate of dissolution of the quartz one could take a crystal with definitely known surface and from that calculate how many grams per square centimeter had been dissolved; but when a quartz crystal is dissolved, the dissolution starts at the alternate intersections of the pyramid faces, so that the hexagon pyramid approaches a triangular pyramid. In other words, the dissolving starts not on the surface but along a line, and therefore that method could not be used. Mr. Martin

in England has used crystals, although he had quartz cuboids, which are rather a rare form and which the authors were not able to secure, to check up.

In regard to the silver plating noted by Professor Taggart, a careful manipulation was necessary in order to secure concordant results, as anyone who has dealt with silver-plating solutions knows. In general the two methods gave fairly concordant results as a check on surface.

Perhaps it would be to the point for practical men to say a word on the practical application of this. Possibly it was assumed that we would see instantly its application. The hope was to get data on the exact amount of work required to produce a given surface. We have no criterion as to the accomplishment of the work that has been spent in crushing.

The authors have actually used a drop-weight method and have correlated the expenditure of work for the production of a given surface. They will go out in the mill and see how that checks out in actual practice in grinding, and from that and from the analysis of the factors involved in the mill, they hope to be able to design better crushing machinery, for as we all know, the cost of crushing is the main cost now in flotation.

J. Gross and S. R. Zimmerley (written discussion).—The authors do not agree with Professor Taggart "that all extrapolation is dangerous." If the extrapolated portion of a curve is short, compared to the entire length of the determined curve, especially in the case of flat curves, the danger from extrapolation is not great. In the extrapolation of a straight line there is, of course, no danger. The mathematical expression as applied to the experimental data obtained from the dissolution tests results in the extrapolation of a straight line as shown in Fig. 1, where the straight line $KC + R$ is the one really extrapolated. As this expression fits the experimental data over a wide variety of experiments covering all sizes or mixture of sizes of quartz, and over long periods of time, it certainly seems reasonable that the expression represents the curve with a high degree of accuracy.

Although the distribution of particles from the limit of visibility down to the unit structure of quartz, the triplet, is unknown, the work of Martin and that of Gaudin show a regular gradation in size down to the limit of accuracy for the microscope, and it does not seem reasonable to expect a sharp discontinuity so far from the unit triplet of quartz unless considerable evidence is brought forth to the contrary. From present knowledge, solvation, or any form of increased activity of quartz particles due to their high state of subdivision, would not show an appreciable effect on particles above 0.01 micron in size. If these effects were appreciable, the nature of the dissolution curve would be seriously affected. The dissolution curves obtained in all cases, from very coarse to the finest elutriation overflow, are all of a distinct type to which the mathematical expression applies, and the extrapolation is in all cases, therefore, that of a straight line.

While some of the factors mentioned by Professor Taggart may enter into the final accuracy of the dissolution method, the authors feel that none of them are serious and that they are extremely small compared with the method of estimation previously used.

It is true that fragments of quartz corrode at different rates depending on the orientation of the crystal axis, but where thousands of such fragments are present the results are statistically true, and if $n$ particles are present, representing $n$ times the surface, a corresponding amount will be dissolved in unit time.

The data presented in papers II and III (pp. 27 and 35) further substantiate the dissolution method as a satisfactory means for the measurement of the surface of quartz.

The apparent discrepancy noted with respect to the silver coating may be due to a misunderstanding of the text or to insufficient explanation on the part of the authors.

The thickness of the silver coating does depend on the total surface presented to the solution; *if* two separate samples of quartz are separately treated with the same quantity of solution, the sample with the greater surface will have a thinner coating, *but* when two samples of quartz having different surface areas together with a glass plate or quartz crystals are simultaneously treated in the same solution, the thickness of all coatings will be the same as shown by experiment and as quoted in the text. The use of the factor obtained by silver coating for converting the I. R. value to specific surface gives a definite conception of actual surface which the I. R. value does not do. In using the factor the results are still comparative measurements.

If we "restrict the data upon which statements of comparative surface are to be based to the region in which concordant experimental results are obtainable," we do not have a measure of surface as explained on page 3 of the text. The authors are pleased to see that Professor Locke agrees with them in regard to the extrapolation.

Professor Locke asks why the quartz was not preheated as well as the solution in making the dissolution test. If the room temperature varies much from the 25° C., the quartz is brought to the required temperature. Ordinarily a few degrees difference in temperature of the quartz may be neglected. Due to the low specific heat of quartz a difference of 2° C. in the temperature of the quartz added would result in a change of 0.06° C. in the temperature of the solution, which would then only be for a short duration of time.

[For additional discussion, see page 44.]

# Crushing and Grinding, II.—Relation of Measured Surface of Crushed Quartz to Sieve Sizes*

By John Gross† and S. R. Zimmerley,‡ Salt Lake City, Utah

(New York Meeting, February, 1929)

The deductions drawn in crushing and grinding operations have heretofore been based on a separation of the products into various sizes. A crushed product may be sized by sieving, by elutriation and by aid of the microscope. To estimate the surface of each size the relation of the surface to the estimated average diameter must be assumed. Such a relation, owing to the irregularity of the particles, may involve two assumptions: First, a factor to convert average diameter to surface for one particular size; and second, a variation in the factor as the diameter of the particle changes. Obviously a surface measurement in which such assumptions and estimates are involved is questionable.

In the first paper of this series[1] a method has been given by which an accurate measure of surface of quartz can be obtained from its dissolution rate. By the use of this method, surface measurements have been made on a series of sieve sizes of crushed quartz, the results of which are given and discussed in this paper.

## Preparation of the Quartz Sizes

The quartz, consisting of large uniform pieces with a density of 2.65 and a purity of 99.5 per cent. $SiO_2$, was crushed to pass 20 mesh and was then sieved. Tyler standard sieves were used, the sieving being done by hand according to the proposed standard method submitted by the senior author to the Milling Committee of the A. I. M. E. A wet split of the sample was made on a 270-mesh sieve. This was followed by dry sieving until less than 0.05 per cent. of the weight of the sample passed through the sieve in 1-min. sieving. The +28-mesh material was discarded because that size did not contain the difficult grains from the 20-mesh sieve.

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* Published by permission of the Director, U. S. Bureau of Mines.

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[1] J. Gross and S. R. Zimmerley: Crushing and Grinding, I.—Surface Measurement of Quartz Particles. See page 7.

The material of each sieve size was cleaned by removing abraded iron with a magnet and then by a treatment with hot nitric and hydrochloric acids. After being thoroughly washed and dried, the samples were bottled. As results were later desired on sieve sizes coarser than 28 mesh, a lot of the same quartz was crushed to pass a 9.423-mm. sieve and was sieved in the same manner as the first lot.

## Relation of Measured to Theoretical Surface

The results obtained in the measurement of surface on the various sizes of quartz products are given in Table 1. In the dissolution tests two different ratios of solvent to solid were used for the finer sizes as a check. The "average size" of a sieve-sized product depends on whether the average is based on size, on surface, or on weight of the particles, and on whether the limiting sizes are weighted. For the purpose of comparing measured to theoretical surface the "average size" is taken as the mean of the limiting sieve sizes.

The theoretical surface is calculated for 1 g. of spheres with a diameter equal to the average size, or for 1 g. of cubes with an edge equal to the average size, as the surface *per gram* is equal for both spheres and cubes. All surfaces are calculated to square centimeters per gram.

Table 1.—*Data on Sieve Sizes of Crushed Quartz*

| Mesh | Average Size of Particle, Mm. | Theoretical Surface per Gram of Quartz Cubes or Spheres, Sq. Cm. | Initial Rate, I. R. | Measured Surface per Gram, Sq. Cm. I. R. × 170 | Ratio of Measured to Theoretical Surface |
|---|---|---|---|---|---|
| 3/4 | 5.690 | 4.0 | 0.201 | 34.2 | 8.55 |
| 4/6 | 4.013 | 5.65 | 0.258 | 43.9 | 7.77 |
| 6/8 | 2.845 | 8.0 | 0.307 | 52.2 | 6.53 |
| 8/10 | 2.007 | 11.3 | 0.351 | 59.7 | 5.28 |
| 10/14 | 1.410 | 16.0 | 0.425 | 72.3 | 4.52 |
| 14/20 | 1.001 | 22.5 | 0.525 | 89.3 | 3.97 |
| 20/28 | 0.711 | 31.8 | 0.632 | 107.4 | 3.38 |
| 28/35 | 0.503 | 45.0 | 0.823 | 139.9 | 3.11 |
| 35/48 | 0.356 | 63.5 | 1.038 | 176.5 | 2.78 |
| 48/65 | 0.252 | 90.0 | 1.393 | 236.8 | 2.63 |
| 65/100 | 0.178 | 127.0 | 1.851 | 314.7 | 2.48 |
| 100/150 | 0.126 | 180.0 | 2.504 | 425.7 | 2.37 |
| 150/200 | 0.089 | 254.0 | 3.219 | 547.2 | 2.15 |
| 200/270 | 0.063 | 360.0 | 4.287 | 728.8 | 2.02 |

As the average size of −270-mesh product varies greatly with the manner of crushing, the theoretical surface cannot be calculated, and the results are therefore not included in Table 1. The importance of

the finest material produced in a crushing or grinding operation is such that material finer than 200 mesh is considered separately.

The ratios of measured to theoretical surfaces are plotted in Fig. 1 against the average size of particle. The data in Table 1 and the curve in Fig. 1 show a remarkable increase in the ratio of measured to theoretical surface with coarser sizes; if these data are correct, an estimate of sur-

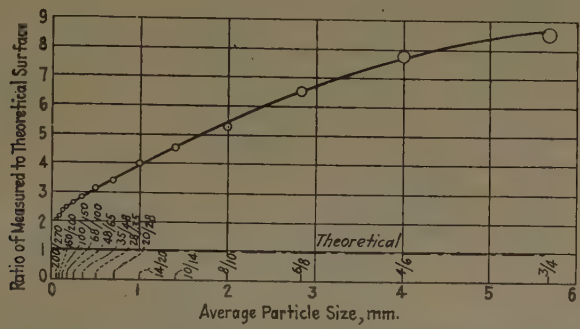


FIG. 1.—RATIO OF MEASURED TO THEORETICAL SURFACE OF CRUSHED QUARTZ. (Size of circle represents a possible error of 2.5 per cent. either way.)

face based on a constant relation of sieve size is not possible. Although other crushed material or quartz, if crushed differently, may not show such a wide difference between the finer and coarser sizes, the results obtained are so unexpected that it is advisable to examine the data for their reliability and to discuss the reasons for this remarkable condition.

## RELIABILITY OF THE DATA

The accuracy of the dissolution method was discussed in the first paper of this series. The present discussion refers more particularly to the reliability of the method when applied to coarse as well as to fine material. This will be discussed from two standpoints:

(a) The measured surface on Ottawa sand;

(b) The logarithmic relation of the measured surface to the average size.

### *The Measured Surface on Ottawa Sand*

If the dissolution method of surface measurement is reliable, determinations made on sieve sizes of perfect spheres or cubes should show a constant relation to the theoretical surface. Perfect spheres or cubes are impossible to obtain, but an approximation is found in the Ottawa sand, which is of high purity and consists of spheres fairly regular in shape, although not perfectly smooth. With such a sand, a surface value somewhat higher than the theoretical one, but with a nearly constant relation to it, would be expected.

A sample of Ottawa sand was cleaned by nitric and hydrochloric acids and finally by hydrofluoric acid to dissolve any silica coating, and was then sieved in the same manner as the crushed material. Initial rates were determined by the dissolution method on the various sizes.

Results with the Ottawa sand are given in Table 2 and show that the ratio of measured to theoretical surface is nearly a constant, with

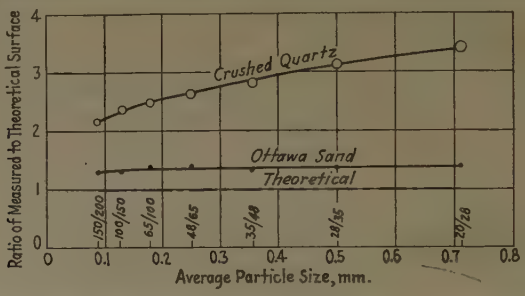


FIG. 2.—RATIO OF MEASURED TO THEORETICAL SURFACE FOR CRUSHED QUARTZ AND OTTAWA SAND.
(Size of circles represents a possible error of 2.5 per cent. either way.)

perhaps a slight increase for the coarser sizes. As the dissolution method, then, gives surface measurements on various sizes of approximate spheres consistent with the theoretical surface of perfect spheres, this fact may be taken as a proof of its accuracy. In Fig. 2 the results obtained on the Ottawa sand are plotted in comparison to similar sizes of crushed quartz.

TABLE 2.—*Data on Sieve Sizes of Ottawa Sand*

| Mesh | Average Size of Particle, Mm. | Theoretical Surface per Gram of Quartz Spheres, Sq. Cm. | Initial Rate, I. R. | Measured Surface per Gram, Sq. Cm. I. R. × 170 | Ratio of Measured to Theoretical Surface |
|---|---|---|---|---|---|
| 20/28 | 0.711 | 31.8 | 0.255 | 43.4 | 1.37 |
| 28/35 | 0.503 | 45.0 | 0.358 | 60.9 | 1.35 |
| 35/48 | 0.356 | 63.5 | 0.497 | 84.5 | 1.33 |
| 48/65 | 0.252 | 90.0 | 0.732 | 124.4 | 1.38 |
| 65/100 | 0.178 | 127.0 | 1.020 | 173.4 | 1.37 |
| 100/150 | 0.126 | 180.0 | 1.386 | 235.6 | 1.31 |
| 150/200 | 0.089 | 254.0 | 1.923 | 326.9 | 1.29 |

### *Logarithmic Relation of Measured Surface to Average Size*

In Fig. 3, the logarithm of measured surface (square centimeters per gram) is plotted against the logarithm of average size of particle (in microns) for various sieve sizes of crushed quartz and Ottawa sand.

If these curves are extended into the range of finer sizes, the ultimate point will be that of a unit crystal of quartz. The unit of structure of a quartz is taken as the quartz triplet, a triangular prism having edges of

5.4 Å. and 4.9 Å. On this basis, the calculated surface of the ultimate particles is 66,500,000 sq. cm. per gram.

From this datum, the point for the unit crystal is plotted in Fig. 3, and the curves for crushed quartz and Ottawa sand are extended to it.

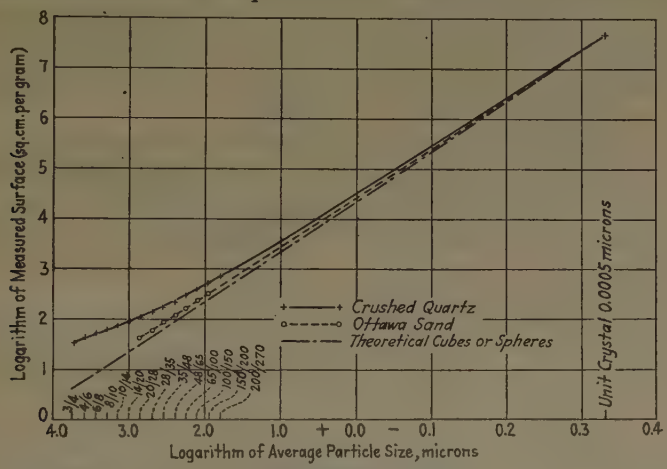


FIG. 3.—LOGARITHMIC RELATION OF MEASURED SURFACE OF QUARTZ TO AVERAGE PARTICLE SIZE.

The Ottawa sand, due to its regularity in shape, gives points that lie in a straight line to the unit crystal point, but the points for the crushed quartz have a slight curvature. That these curves extend so nicely to the ultimate particle may be taken as further evidence of the accuracy of the surface measurements.

## THE HIGH RATIO OF MEASURED SURFACE ON COARSER PARTICLES

An examination of the curves in Fig. 3 brings out the two points that the curve for Ottawa sand follows the theoretical curve, but that the curve for crushed quartz departs from it in the range of the coarser sizes, showing that with increased size in the particles of crushed quartz, a greater measured surface is obtained than would be expected. There may be two causes for this effect: (a) A change of configuration in the particles; (b) cracks in the particles.

### *A Change of Configuration*

That quartz particles, as they become smaller, approach spheres in shape is a plausible theory. A gradually increasing irregularity with increasing size would account for a deviation from the theoretical line in Fig. 3.

### *Cracks in the Particles*

Experiments indicate that the greater part of the increased measured surface on coarser particles is due to cracks or interior surface in the

quartz. Microscopic examination of crushed quartz shows clearly the increased number of cracks with the increased size of particles. When crushed quartz is treated with strong hydrofluoric acid the cracks become noticeable. Dissolution takes place within the cracks to such an extent that finally a separation of the particle occurs. This action is slight on finer sizes, but it is very pronounced on coarser sizes; this result not only verifies the conclusion from microscopic examination, but also shows that dissolution actually takes place in the cracks.

A more definite proof that cracks result in a greater surface value was obtained by silver-coating crushed quartz. By this method no coating is formed in the cracks, and the surface measurement represents only exterior surface. A number of sizes of crushed quartz were silver-coated; the results are given in Table 3.

TABLE 3.—*Data on Surface Measurements of Crushed Quartz by Dissolution and by Silver Coating*

| Mesh | Theoretical Surface per Gram of Quartz Cubes or Spheres, Sq. Cm. | By Dissolution | | By Silver Coating | | Ratio of Interior to Outer Surface |
|---|---|---|---|---|---|---|
| | | Measured Surface, Sq. Cm. per Gram | Ratio of Measured to Theoretical Surface | Measured Surface, Sq. Cm. per Gram | Ratio of Measured to Theoretical Surface | |
| 150/200 | 254 | 547.2 | 2.15 | 493.0 | 1.94 | 0.110 |
| 65/100 | 127 | 314.7 | 2.48 | 252.9 | 1.99 | 0.244 |
| 35/48 | 63.5 | 176.5 | 2.78 | 122.1 | 1.92 | 0.446 |
| 20/28 | 31.8 | 107.4 | 3.38 | 59.1 | 1.86 | 0.817 |
| 10/14 | 16 | 72.3 | 4.52 | 36.0 | 2.25 | 1.008 |
| 6/8 | 8 | 52.2 | 6.53 | 18.6 | 2.33 | 1.807 |
| 3/4 | 4 | 34.2 | 8.55 | 9.4 | 2.35 | 2.638 |

The results in Table 3 as plotted in Fig. 4 show that the outer surface measurements obtained by silver-coating follow the theoretical ratio closely; this indicates that there is little change in configuration of particles of various sizes, but that the difference between measured and theoretical surface of crushed quartz is due almost entirely to internal surface.

The dissolution method of surface measurement, therefore, takes into account not only the outer but also the internal surface or cracks. It is not known to what extent this internal measurement approaches completeness, and no method of ascertaining it appears to be available; the only statement that can be made is that internal fractures increase the amount of surface measured in dissolution, and that judging from the rapidity of the disintegration of coarse quartz particles in strong hydrofluoric acid, a fairly high percentage of the internal fractures is measured. As these fractures represent work already done on the particles, it is proper that their surface, as well as the outer surface, should be measured.

The Ottawa sand curve which parallels the theoretical one in Fig. 3 indicates a lack of internal fractures, and microscopic examination confirms this.

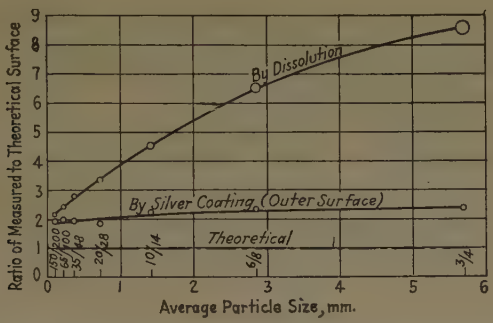


FIG. 4.—EFFECT OF FRACTURES (CRACKS) ON SURFACE MEASUREMENT OF QUARTZ BY THE DISSOLUTION METHOD.
(Size of circles represents a possible error of 2.5 per cent. either way for dissolution and a possible error of 5 per cent. either way for silver coating.)

## *The Minus* 200-*mesh Material*

Although the ratio of measured to theoretical surface is very large for the coarser sizes of quartz, this fact is not of great importance in the study of crushed or ground products. The −200-mesh material, because of its large surface, usually represents the major part of the work in crushing; it is, therefore, of greater importance to measure and study the finer sizes of a crushed product.

It has been the custom to assume that −200-mesh material has an average size of 37 microns, the mean between the opening in the 200-mesh sieve and zero. From Fig. 3 the average size of a sample of crushed quartz may be obtained when the measured surface has been determined. The lowest and highest values obtained so far for −200-mesh crushed quartz is 2043 sq. cm. per gram and 7055 sq. cm. per gram respectively; the average sizes of the particles, as taken from Fig. 3, were 18 microns and 5 microns respectively. These figures show that an assumed value of 37 microns for such material is seriously in error.

The −200-mesh quartz which gave the 5-micron average size was obtained from one of the experiments made by A. M. Gaudin,[3] who estimated the average size as equal to 2 microns. Gaudin's figure makes the assumed average of 37 microns appear still more incorrect.

The foregoing discussion on −200-mesh material indicates that a great deal of useless work may be represented by material finer than that necessary for metallurgical requirements. If a product is desired that just passes a certain mesh, the ideal crushing is that which produces just this size and no smaller. From Fig. 3, the surface of 1 g. of crushed

[3] A. M. Gaudin: An Investigation of Crushing Phenomena. *Trans.* A. I. M. E. (1926) **73,** 253.

quartz of this size may be found. The surface having been determined on material finer than the desired size, an index of the useful work performed may be obtained.[4] If $S'$ = the square centimeter of surface determined and $S$ = the square centimeter of surface for ideal crushing, then $\frac{S \times 100}{S'}$ = the index of useful work where 100 represents a product containing no particles smaller than the size desired.

Considering the smallest and largest measured surfaces obtained on −200-mesh quartz—that is, 2043 and 7055 sq. cm. per gram—this formula gives an index of useful work of 30 per cent. and 8.8 per cent. respectively. The latter figure indicates a large amount of useless work, if particles of 74 microns are fine enough.

## Summary

The calculation of surface for quartz based on average size as obtained by sieve sizing is subject to serious error. Surface measurements of sieve sizes of crushed quartz show that the ratio of measured to theoretical surface is large for coarser particles and gradually diminishes as the particles become finer. This difference is due almost entirely to fractures, the surfaces of which are measured in part, and probably to a large extent, by the dissolution method.

The surface measurements of sieve sizes of Ottawa sand show a fairly constant ratio of measured to theoretical surface, because this sand is practically free from fractures. The outer surface of sieve sizes of crushed quartz also shows a fairly constant ratio of measured to theoretical surface. The graph showing the logarithmic relation between surface per unit weight and size of particle may be extended to the unit crystal of quartz as a slight curve for crushed quartz and as a straight line for Ottawa sand. From this graph the average size of particles may be obtained for any sample of quartz after the surface has been determined.

The constant relation of the measured to theoretical surface for Ottawa sand and for the outer surface of crushed quartz, and the extension to unit crystals of the logarithmic relation of surface to size of particle, are considered as further evidence of the accuracy of the dissolution method for surface determinations.

The −200-mesh material is of greater importance than the coarser sizes in the study of crushing and grinding operations. The average size of particles in a −200-mesh crushed product is usually much smaller than 37 microns.

Much of the work in crushing and grinding is expended in producing finer material than is required. By the measurement of surface of crushed material, an index of the useful work may be ascertained.

[For discussion, see page 44.]

[4] The third paper of this series, page 35, gives the evidence that surface produced is a direct measure of work expended in crushing.

# Crushing and Grinding, III.—Relation of Work Input to Surface Produced in Crushing Quartz*

By John Gross† and S. R. Zimmerley,‡ Salt Lake City, Utah

(New York Meeting, February, 1929)

The method of measurement of surface on quartz particles was given in a previous paper.[1] With such a method the relation of surface produced in crushing quartz can be compared to the work in crushing without recourse to sieve sizing or microscopic measurement.

In crushing, the work input must be known with a fair degree of accuracy. With crushers, rolls, ball mills, and similar apparatus the measurement of the work in crushing is subject to possible errors, due to friction in the transmission as well as in the machine itself. Moreover, relatively large quantities of material must be crushed to get an average figure. In the selection of a method of crushing, simplicity in design and operation was desired and this was most readily obtained by the use of a free-falling body. A description of the apparatus embodying this principle is given herewith.

## The Crushing Device

The apparatus used is shown in Fig. 1 and in cross-section in Fig. 2. The material to be crushed is placed in the crushing chamber $C$ in the steel mortar $M$. The mortar is 3 in. dia. by 3 in. high. Two mortars are used, one having a crushing chamber 1 in. dia. by ½ in. deep, with a capacity of 4 g. of quartz, the other having a crushing chamber 1½-in. dia. by ¾ in. deep, with a capacity of 12 g. of quartz. The position of the mortar is adjusted by means of three centering screws $A$.

The steel plunger $P$, which fits neatly into the chamber, is placed on top of the material to be crushed. Plungers of different lengths were tried and as they were found to give practically identical results the length adopted was equal to the depth of the chamber.

The mortar rests on a solid steel base $B$ but is separated therefrom

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‡ Assistant Metallurgist, Intermountain Experiment Station, U. S. Bureau of Mines.

[1] J. Gross and S. R. Zimmerley: Crushing and Grinding, I.—Surface Measurement of Quartz Particles. (See page 7.) This method is based upon the rate of dissolution of quartz in hydrofluoric acid. The initial rate of dissolution is a measure of the surface and is designated as I. R.

by three standard aluminum wires *W*. The base consists of a steel block 6 in. dia. by 8 in. high, set on a concrete column 3 ft. high. The aluminum wires prevent rebound of the ball and by their deformation, or flattening, give the measure of work not used in crushing.

The weight, a steel ball, is supported by a cord at the desired height. An adjustable crossbar, which can be raised or lowered, allows the cord to rest in the center line of the apparatus. When the ball is perfectly quiet the cord is cut just above the crossbar. By cutting the cord at this point the ball is not thrown out of alignment.

The apparatus is built to give a maximum fall of 60 cm. The weight of the balls used was 1.360, 2.050, and 2.935 kilograms.

Fig. 1.—Crushing apparatus.

## Net Work Going to Crushing

With a definite weight and a drop of definite distance, a definite amount of work is delivered upon impact. If the mortar rests solidly on the base a rebound of the ball takes place, the measure of which represents loss of work. Attempts to

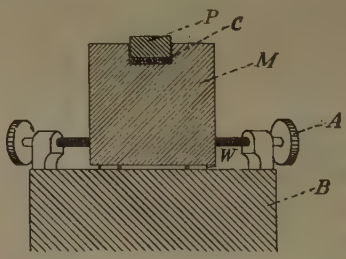


Fig. 2.—Cross-section of crushing apparatus.

measure accurately the rebound of the ball proved to be difficult and cumbersome. The best method was that of taking photographs with an exposure covering the total time of rebound. The photograph showed the path of the ball with its highest point of rebound,and by means of a scale this could be meaured and a relationship obtained to the work input. While the photographic method could have been used, it was not desirable when hundreds of crushing tests were to be made. As it was not always possible to obtain a satisfactory photograph, repeat crushings would often have been necessary, with the attendant delay.

If an inelastic substance, which will readily deform, is placed between the mortar and base, no rebound of the ball takes place and the deformation gives a means of measuring the transmitted downward forces.

The selection of the deformable substance depends on the force of impact by the falling ball; it must deform sufficiently to prevent rebound and must resist sufficiently to give as high an efficiency in the utilization of the work in crushing as possible.

After many trials with lead shot, fuse wire, aluminum wire and copper wire, aluminum wire was selected because it fulfilled all the requirements and could be obtained in dependable uniformity. Three aluminum wires, 3.232 mm. dia., cut to lengths of exactly 1 cm., are used. These are

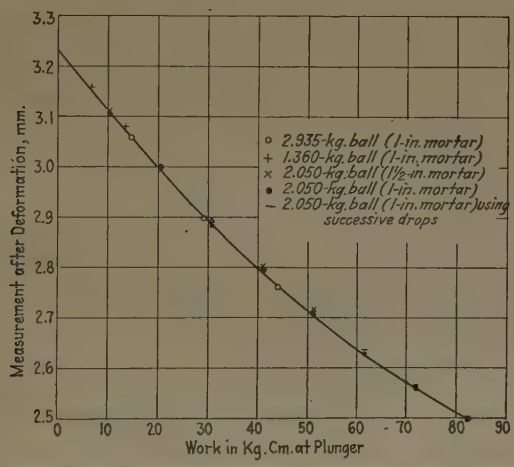


FIG. 3.—WORK IN KILOGRAM-CENTIMETERS AT PLUNGER FOR DEFORMATION OF THREE 1-CM. ALUMINUM WIRES 3.232-MM. DIAMETER.

placed radially 120° apart between the mortar and the base. From the deformation of these wires the work not expended in crushing is obtained.

A portion of the work resulting from the impact of the falling ball accomplishes a certain deformation of the three aluminum wires between the mortar and the base. This deformation is a measure of the total work of the falling ball if no crushing is done. If crushing is done, the deformation is a measure of the work not utilized.

## CALIBRATION OF THE WIRES

The relation of the deformation of the wires to the total work when no crushing is done gives a smooth curve. Such a calibration curve was obtained for aluminum wires where the weight of ball and the height of drop were varied, and also where successive drops were made on the same set of wires. Two different mortars were also used. This calibration curve is shown in Fig. 3, the points of which are averages of all experiments in Table 1. In this table all of the deformation figures obtained are given to show the close agreement under varying conditions. This curve was used in all crushing experiments.

TABLE 1.—*Measurement after Deformation of Three 1-cm. Aluminum Wires 3.232 Mm. Diameter*

1.360-KG. BALL—1-IN. MORTAR

| 5-CM. DROP 6.80 KG. CM. | 10-CM. DROP 13.60 KG. CM. |
|---|---|
| 3.153 | 3.080 |
| 3.162 | |
| 3.157 | 3.080 |

2.050-KG. BALL—1-IN. MORTAR

| 5-CM. DROP 10.25 KG. CM. | 10-CM. DROP 20.50 KG. CM. | 15-CM. DROP 30.75 KG. CM. | 20-CM. DROP 41.000 KG. CM. | 25-CM. DROP 51.25 KG. CM. | 30-CM. DROP 61.50 KG. CM. | 35-CM. DROP 71.75 KG. CM. | 40-CM. DROP 82.00 KG. CM. |
|---|---|---|---|---|---|---|---|
| 3.105 | 2.985 | 2.887 | 2.798 | 2.712 | 2.627 | 2.572 | 2.502 |
| 3.105 | 2.988 | 2.882 | 2.793 | 2.705 | 2.630 | 2.555 | 2.488 |
| 3.105 | 2.988 | | | | | 2.553 | |
| 3.105 | 2.987 | 2.885 | 2.796 | 2.709 | 2.629 | 2.560 | 2.495 |

2.050-KG. BALL—1½-IN. MORTAR

| 5-CM. DROP 10.25 KG. CM. | 10-CM. DROP 20.50 KG. CM. | 15-CM. DROP 30.75 KG. CM. | 20-CM. DROP 41.00 KG. CM. | 25-CM. DROP 51.25 KG. CM. |
|---|---|---|---|---|
| 3.132 | 3.003 | 2.902 | 2.798 | 2.722 |
| 3.108 | 3.012 | 2.892 | 2.802 | 2.708 |
| 3.115 | 2.995 | 2.902 | 2.800 | |
| 3.110 | 2.993 | 2.902 | | |
| 3.107 | 2.987 | 2.883 | | |
| 3.108 | | 2.888 | | |
| 3.113 | 2.998 | 2.895 | 2.800 | 2.715 |

2.935-KG. BALL—1-IN. MORTAR

| 5-CM. DROP 14.68 KG. CM. | 10-CM. DROP 29.36 KG. CM. | 15-CM. DROP 44.04 KG. CM. |
|---|---|---|
| 3.068 | 2.897 | 2.763 |
| 3.060 | | |
| 3.052 | | |
| 3.060 | 2.897 | 2.763 |

2.050-KG. BALL—1-IN. MORTAR—SUCCESSIVE DROPS

| 15-CM. DROP 30.75 KG. CM. | 15 + 5-CM. DROP 41.00 KG. CM. | 15 + 5 + 5-CM. DROP 51.25 KG. CM. | 15 + 5 + 5 + 5-CM. DROP 61.50 KG. CM. | 15 + 5 + 5 + 5 + 5-CM. DROP 71.55 KG. CM. | 15 + 5 + 5 + 5 + 5 + 5-CM. DROP 82.00 KG. CM. |
|---|---|---|---|---|---|
| 2.888 | 2.792 | 2.720 | 2.633 | 2.575 | 2.503 |
| 2.893 | 2.795 | 2.710 | 2.640 | 2.563 | 2.507 |
| | | 2.708 | 2.638 | 2.565 | 2.492 |
| | | 2.720 | 2.635 | 2.565 | 2.508 |
| | | | | 2.558 | 2.498 |
| | | | | 2.577 | 2.497 |
| 2.891 | 2.794 | 2.715 | 2.637 | 2.567 | 2.501 |

## Procedure for the Crushing Tests

The amount of quartz to be crushed is accurately weighed to within 0.1 mg.; it is placed in the crushing chamber, leveled evenly on top of charge, and moistened with absolute alcohol, and the plunger is set in place. The mortar is carefully placed upon the three standard aluminum wires. The exact position of the mortar is maintained by a previous adjustment of the three centering screws.

The ball is now suspended, the height of drop being measured by means of a gage. By anchoring the suspending cord, the ball is held securely in place and is allowed to come to complete rest. A cylindrical apron is placed around the mortar to catch any material that may be thrown outward. The ball is allowed to drop by cutting the cord just above the crossbar. The mortar is taken up, the plunger removed and brushed clean, and the chamber cleaned out.

The function of the alcohol is to prevent dust loss; it evaporates rapidly enough so that the removal of the crushed material from the chamber is not unduly prolonged. As the surface measurements are based on the weight of the material before crushing, dust loss may be a serious item. To prevent this the alcohol moistening was introduced, which keeps the loss down to less than 0.10 per cent. in weight.

The deformation of each of the three standard aluminum wires is now measured by micrometer and averaged. The work represented by this deformation is obtained from the calibration curve.

The figures obtained in duplicate experiments for net work going to crushing check remarkably closely. A poorly centered drop is immediately noticed by the unequal deformation of the wires. As six or more samples are required for the measurement of surface by the dissolution method, a sufficient number of crushings under identical conditions must be made for each experiment. In some experiments each individual crushing was taken as a sample for dissolution and in others two crushings were combined. In two experiments a large number of crushed samples were combined, sized by sieves, and the surface determined on the several sieve sizes.

## Surface Determination on Mixed Sizes

As the surface determinations were to be made on the crushed samples without sizing it was desirable to ascertain whether a mixture of sizes gave an accurate surface measurement. This investigation covered material within the sieve range and material finer than the sieve scale.

A composite sample of crushed quartz was prepared from sieve-sized samples, the results of which have been given previously.[2] The data

[2] J. Gross and S. R. Zimmerley: Crushing and Grinding, II.—Relation of Measured Surface of Crushed Quartz to Sieve Sizes. See page 27.

for this composite are given in Table 2. Two surface determinations on the composite sample gave 251.4 and 251.1 sq. cm. per gram, an average of 251.25, checking the surface obtained by the individual I. R. determinations (252.25) within 0.4 per cent.

TABLE 2.—*Data for Composite Quartz Sample within the Sieve Scale*

| Sieve Size | Per Cent. Weight in Composite | Initial Rate (I. R.) | Surface, Sq. Cm. per Gram (I. R. × 170) | Surface × Per Cent. Weight |
|---|---|---|---|---|
| 28/35 | 32.0 | 0.823 | 139.9 | 4,476.8 |
| 35/48 | 23.0 | 1.038 | 176.5 | 4,059.5 |
| 48/65 | 16.0 | 1.393 | 236.8 | 3,738.8 |
| 65/100 | 11.5 | 1.851 | 314.7 | 3,619.1 |
| 100/150 | 8.0 | 2.504 | 425.7 | 3,405.6 |
| 150/200 | 5.5 | 3.219 | 547.2 | 3,009.6 |
| 200/270 | 4.0 | 4.287 | 728.8 | 2,915.2 |
| Average..... | | 1.487 | 252.25 | 25,224.6 |

A similar experiment was made on −200 crushed quartz which had been separated into four products by elutriation, surface determination having been made on each elutriation product as well as on the original material. The results are given in Table 3. Three surface determina-

TABLE 3.—*Data for Elutriation Products of Minus* 200 *Crushed Quartz*

| Product | | Per Cent. Weight of Original | Initial Rate (I. R.) | Surface, Sq. Cm per Gram (I. R. × 170) | Surface × Per Cent. Weight |
|---|---|---|---|---|---|
| Rising in Upward Current | Not Rising in Upward Current | | | | |
| Mm. Per Second | | | | | |
| (200 mesh) | 1.92 | 45.91 | 5.370 | 913 | 41,916 |
| 1.92 | 0.48 | 36.05 | 12.375 | 2,104 | 75,849 |
| 0.48 | 0.12 | 8.45 | 31.080 | 5,284 | 44,650 |
| 0.12 | 0.00 | 9.58 | 128.703 | 21,880 | 209,610 |
| Averages..... | | | 21.882 | 3,720 | 372,025 |

tions on the original −200-mesh material gave 3609, 3711, and 3754 sq. cm. per gram, an average of 3691, checking the surface obtained by the individual I. R. determinations within 0.8 per cent. The results of the two preceding experiments indicate that a mixture of sizes gives accurate results and that the surface may, therefore, be measured directly on the crushed material without recourse to sizing. This was further verified in crushing experiment I, results of which are given later, in

which the average surface obtained by the individual I. R. determinations on each size was 343.4 sq. cm. per gram and the determination on the composite sample was 337.1 sq. cm. per gram, a difference of 1.8 per cent.

## The Crushing Tests

Crushing tests were made with quartz of various sizes, with different amounts of quartz, with different work input and with different crushing mortars. The various experiments made are reported herewith in Table 4. In the last column of this table the new surface produced per kilogram-centimeter of work input is given; these figures fall within the allowable error by the Chauvenet criterion. They show that in the machine used, 17.56 sq. cm. of quartz surface is produced for each kilogram-centimeter of work input in crushing.

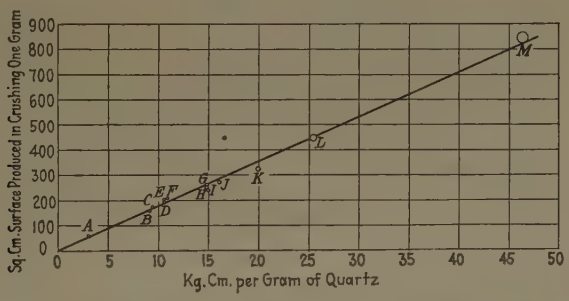


Fig. 4.—Relation of work input to surface produced in crushing quartz. (Size of circles indicates a possible error of 2.5 per cent. either way.)

The results are shown in Fig. 4, the work expended in crushing being plotted against the new surface produced. These points fall very close to a straight line going through zero. It follows, therefore, that these tests show that the Rittinger law, "The work of crushing is directly proportional to the new surface produced," is correct.

It will be seen from Fig. 4 that the points for experiments I and K are farther from the straight line than the others. This is to be expected from the nature of the experiments. In all of the experiments except I and K dissolution tests were made directly on the crushed products and were based on the original weight of material. Any loss in weight during crushing, therefore, is counted as dissolved silica in the dissolution test. In experiments I and K the crushed products from a large number of individual crushings were combined and sieved. Dissolution tests were then made on weighed portions of the sized products. It may be presumed that crushing and sizing losses are largely made up of very fine dust with a high surface value per unit weight; this would result in an I. R. value somewhat too low for experiments I and K.

TABLE 4.—*Data on Quartz Crushing Tests*

| Exp. No. | Sieve Size of Quartz before Crushing | Grams Crushed Each Crushing | Grams Crushed for Dissolution Tests | Crushing Chamber | Data on Work in Crushing | | | | | Surface per Gram Sq. Cm. (I. R. × 170) | | | Surface Produced Sq. Cm. per Kg-cm. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Weight of Ball, Kg. | Drop, Cm. | Total Kg-cm. per Gram | Net Kg.-cm. per Gram to Crushing | Per Cent. of Work. Input to Crushing | Crushed Product | Before Crushing | Net Due to Crushing | |
| A | 10/14 | 12 | 72 | 1½ × ¾ | 2.050 | 20 | 3.42 | 3.02 | 88.4 | 129.7 | 72.3 | 57.4 | 19.0 |
| B | 10/14 | 4 | 64 | 1 × ½ | 2.050 | 20 | 10.25 | 9.21 | 89.9 | 227.1 | 72.3 | 154.8 | 16.8 |
| C | 10/14 | 4 | 20 | 1 × ½ | 2.050 | 20 | 10.25 | 9.37 | 91.4 | 249.6 | 72.3 | 177.3 | 18.9 |
| D | 35/48 | 4 | 80 | 1 × ½ | 2.050 | 30 | 15.37 | 10.64 | 69.2 | 393.4 | 200.4 | 193.0 | 18.1 |
| E | 35/48 | 4 | 40 | 1 × ½ | 2.935 | 20.95 | 15.37 | 10.64 | 69.2 | 400.0 | 200.4 | 199.6 | 18.8 |
| F | 35/48 | 4 | 72 | 1 × ½ | 1.360 | 45.22 | 15.37 | 10.82 | 70.4 | 406.5 | 200.4 | 206.1 | 19.0 |
| G | 10/14 | 4 | 48 | 1 × ½ | 2.050 | 20+20 | 20.50 | 14.77 | 72.1 | 328.1 | 72.3 | 255.8 | 17.3 |
| H | 20/28 | 4 | 32 | 1 × ½ | 2.050 | 40 | 20.50 | 14.79 | 72.1 | 349.2 | 97.4 | 251.8 | 17.0 |
| I | 20/28 | 4 | 296 g. sized | 1 × ½ | 2.050 | 40 | 20.50 | 15.04 | 73.4 | 340.3 | 97.4 | 242.9 | 16.2 |
| J | 10/14 | 4 | 56 | 1 × ½ | 2.050 | 40 | 20.50 | 16.12 | 78.6 | 343.1 | 72.3 | 270.8 | 16.8 |
| K | 65/100 | 3 | 108 g. sized | 1 × ½ | 2.050 | 50 | 34.17 | 19.85 | 58.1 | 690.2 | 369.8 | 320.4 | 16.1 |
| L | 10/14 | 4 | 96 | 1 × ½ | 2.050 | 40+40 | 41.00 | 25.43 | 62.0 | 518.2 | 72.3 | 445.9 | 17.5 |
| M | ¾ | 2 | 16 | 1½ × ¾ | 2.935 | 40 | 58.70 | 46.45 | 79.1 | 878.4 | 34.2 | 844.2 | 18.2 |
| | | | | | | | | 206.15 | | | | 3620.0 | 17.56 |

The close agreement obtained in the experiments as to the surface produced per kilogram-centimeter would indicate that, if dust loss is carefully controlled, reasonably reliable results are obtainable either by counting the dust loss in crushing as silica dissolved in the dissolution test, or by adjusting losses in the sieve analysis and determining the I. R. value on known weights of sized material.

## Efficiency of Crushing

Two investigators on the subject of crushing, Gaudin[3] and Martin,[4] have estimated the absolute efficiency of crushing. Their calculations have been based on the surface energy of quartz. They assume the surface energy to be the minimum work theoretically necessary to produce a unit of surface by crushing. Gaudin, using Edser's value as 920 ergs per sq. cm., found that in crushing with rolls 1.3 per cent. of the energy input was represented by the surface produced. Martin calculated the surface energy of quartz to be $\frac{1}{27}$ ft-lb. per sq. ft., which is about 310 ergs per sq. cm. Using this value he found that his ball milling tests showed an efficiency of $\frac{1}{16}$ per cent.

In this investigation it was found that 1 kg-cm. of work produced 17.56 sq. cm. of surface which, when computed on a basis of Edser's surface energy, gave an efficiency of 3 per cent. and upon Martin's value an efficiency of 1 per cent. Although 3 per cent. efficiency may be small, it is large compared with the $\frac{1}{16}$ per cent. reported by Martin.

As the values for the surface energy of solids are unsatisfactory at present, some doubt is cast on the value of theoretical efficiencies. The foregoing efficiencies indicate that a large portion of the energy input in the crushing operation is dissipated in the form of heat. If it had been experimentally feasible to measure accurately the heat generated in the crushing experiments it would have been possible to calculate the amount of energy represented by the increased surface of the quartz. An absolute figure for efficiency and for the relationship between this energy and surface produced would have been obtained. However, in a crushing operation the only practical point is the relation between power input and crushing accomplished, which has been the object of this investigation.

## Distribution of the Work in Various Sizes of Crushed Quartz

As the results indicated, the work done in crushing is proportional to surface. The distribution of work input for the various sizes in experiments I and K can be calculated. The results are given in Table 5.

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[3] A. M. Gaudin: An Investigation of Crushing Phenomena. *Trans.* A. I. M. E. (1926) **73**, 253.

[4] G. Martin: Grinding in Ball and Tube Mills. *Trans.* Inst. Chem. Engrs. (1926) **4**, 42.

TABLE 5.—*Distribution of Work Expended on Individual Sizes*

Crushing Experiment I—296 Grams of 20 to 28-mesh Quartz

| Sieve Size | Weight, Grams | Surface, Sq. Cm. | | | Distribution of Work |
|---|---|---|---|---|---|
| | | Crushed Product | Original Material | Due to Crushing | |
| +28 | 124.888 | 14,137 | 12,165 | 1,972 | 2.7 |
| 28/35 | 76.456 | 9,205 | 7,447 | 1,758 | 2.4 |
| 35/48 | 31.713 | 5,220 | 3,089 | 2,131 | 2.9 |
| 48/100 | 35.492 | 10,069 | 3,457 | 6,612 | 9.1 |
| 100/200 | 14.287 | 8,090 | 1,392 | 6,698 | 9.2 |
| −200 | 13.164 | 54,936 | 1,282 | 53,654 | 73.7 |
| Totals..... | 296.000 | 101,657 | 28,832 | 72,825 | 100.0 |
| Crushing Experiment K—108 Grams of 65 to 100-mesh Quartz | | | | | |
| +200 | 88.301 | 34,287 | 32,654 | 1,633 | 4.7 |
| −200 | 19.699 | 40,253 | 7,285 | 32,968 | 95.3 |
| Totals..... | 108.000 | 74,540 | 39,939 | 34,601 | 100.0 |

The results of these two experiments indicate that a large amount of the work expended in crushing goes to making material finer than 200 mesh and that, as pointed out in the second paper of this series, the study of the −200-mesh material is a very important part of the crushing and grinding problem.

## SUMMARY

A crushing device has been developed whereby the net work input to a crushing operation can be accurately determined.

Surface determinations may be made on a crushed quartz sample as such a measurement has been shown to be equal to the sum of the measured surfaces of the component sizes.

The data show that when crushing quartz the new surface produced is in direct proportion to the work input in accordance with the Rittinger law of crushing.

Surface measurements show that the major portion of the work expended, even in comparatively coarse crushing, is represented in the −200-mesh material.

## DISCUSSION

[This discussion refers also to the second paper in the series, which begins on page 27.]

J. H. BATCHELLER, Corvallis, Ore.—When I was with the Tomboy mill in Colorado there was a difference in the hardness of quartz in different parts of the mine. We got more wear out of quartz from certain levels than we did from others, and most of our quartz had threads of rhodonite running through it. When we shut down the

grinding mills and examined the pebbles, the rhodonite was softer than the quartz. The amount of wear where the rhodonite had cut down below the surface of the quartz was deeper in some cases than in others. That raised the question in my mind as to which was the failing one; whether the rhodonite was softer in one case than another and the quartz was standard, or the rhodonite was standard and the quartz varied. To offset that question about the softness of the rhodonite, we did find the quartz varied. On the labor in crushing quartz, do the authors feel that they have a stock sample of material of such quantity and consistency that there is no difference in the behavior of the quartz?

J. Gross.—Yes.

C. E. Locke, Cambridge, Mass.—I was shown the carefully guarded, stored away sacks of their stock of quartz, which I do not think they allow ordinary individuals to see for fear that it might be removed. That is very precious.

J. Gross.—There would be a difference in hardness or crushing resistance of different quartz, but we have been working entirely on quartz from northwestern Utah, and as far as we can tell, it is absolutely the same all the way through. We send for 4 or 5 tons at a time, crush it down to the size we want, sort it and store the different sizes for making up head charges on our crushing tests. This we do by combining definite weights of the different sizes so as to be sure that all our heads are the same. I think all our quartz is the same hardness with the exception of coarse material. Material of ¼ in. dia. will crush more easily than material of 100 mesh, for example, for the simple reason that a considerable amount of crushing has already been done on the coarse material, as evidenced by cracks, the surface of which accounts for the relatively large surface figures for coarser material.

A. M. Gaudin, Salt Lake City, Utah (written discussion).—The three papers by Gross and Zimmerley reflect much credit on their authors for the thoroughness with which the investigation has been conducted: The exacting attention paid to details, however small they be, should constitute a model for accurate fundamental research. The outstanding result of this work is the vindication, on an apparently sound basis, of the so-called Rittinger law of crushing, which calls for the production of new surface in proportion to the work input.

Many investigators have attempted to test the validity of the fundamental law of crushing, but with the exception of some recent work, they have leaned to reasoning out the respective advantages of the Rittinger or the Kick law rather than experimenting, or else the value of their experimental data has been substantially destroyed by the inaccuracy of the estimates of area on the finer portions of the feed and ground product. In view of the frequently enormous errors involved in the estimation of the surface contained in the −200 mesh material, the recent conclusions of Haultain, Martin, Gaudin, and of Gross and Zimmerley stand practically unchallenged as vindications of the Rittinger theorem.

The authors are justified in stressing the importance of sizing the −200 mesh portion of crushed products in any attempt to ascertain the work done in crushing or in determinations of crushing efficiencies.

It is with pleasure that I note the apparent concordance between my estimate of 2 microns and Gross and Zimmerley's determination of 5 microns, as the average size of a certain −200-mesh ball mill product. In reality these estimates are quite different, the surface per gram indicated by the authors' measurements being but 40 per cent. of that obtained from my calculations. While I am not at all convinced that my calculation is not off by a considerable amount, it seems desirable to call attention to a factor entering in Gross and Zimmerley's dissolution method which

may be influencing their results in such a way as to indicate a larger average size, or smaller specific surface, or smaller initial rate (I. R.) than should be obtained. This possibility of error is restricted to fine material only, let us say material finer than 2 microns or so. In this connection it is desirable to note that the authors' experimental conditions were designed first for material that is coarse when compared with 1-micron particles. In other words, the concentration of hydrofluoric acid in the solution, and the proportion of solids to solution, were so selected as to dissolve a conveniently measurable amount of silica in ½ to 2 hr., yet keeping this amount sufficiently small not to deplete the hydrofluoric acid solution to too great an extent. When the same set of conditions is applied to very fine material, there results a marked disappearance of fine grains in the first few minutes of dissolution, due to the fact that the statistical thickness of silica removed on each grain hardly affects the diameter of a coarse grain yet dissolves completely a fine grain.

Under the experimental conditions employed by the authors, the silica shell dissolved in ½ hr. is of the order of ¼ micron, so that all grains under ½ micron are completely dissolved in that time. It is true, of course, that reduction in size of the coarse grains has brought them to take the place of the fine grains, but this substitution is far from being quantitative, as can be seen by an inspection of Table 6, taken from Lincoln T. Work's dissertation, recently submitted for the doctorate at Columbia University.

TABLE 6

(As given by Lincoln T. Work)

| Size Range, Microns | Number of Particles per Unit, Weight per Micron |
|---|---|
| 0 –0.58 | 69,800,000 |
| 0.58–1.16 | 7,680,000 |
| 1.16–1.74 | 3,680,000 |
| 1.74–2.32 | 1,232,000 |
| 2.32–3.48 | 255,000 |
| 3.48–4.64 | 81,200 |
| 4.64–6.96 | 16,300 |

In view, of the rapidly expanding number of grains per unit range in size, with decreasing size, it is clear that there is a reduction in the surface of the quartz sample, as time progresses, not only due to reduction in the diameter of the grains, but also due to complete dissolution of the finer grains. Reduction in surface due to disappearance of grains in an unsized feed containing, presumably, material ranging in size down to unit crystals, decreases rapidly with time; being, perhaps, enormously large during the first few seconds and comparatively negligible after a few minutes. If such a condition does exist, and it may, the extrapolation method of Gross and Zimmerley may give an initial rate (I. R.) that is substantially too low, even though their extrapolation be entirely justified under other circumstances.

It would seem as though the use of much more dilute hydrofluoric acid solutions, with a proportionately greater amount of solution, would help establish the possibility of error in the I. R., as determined under the usual conditions. It is realized, however, that there are limitations to all methods, and such experimental conditions may be analytically unsuitable.

In his discussion of the first paper (p. 22), Professor Taggart stated that there is a rather definite minimum size of particles in a suspension of ground quartz in water, and he places the minimum size near the limit of visibility of the microscope; that is, near 0.5 micron.

The paper by Dr. L. T. Work contains some figures which, at first sight, support Professor Taggart's contention. Thus, Table 2, page 22, indicates that in the size

range below 0.58 micron there is 0.38 per cent. of ground quartz for an interval of 1 micron, whereas in the size ranges from 0.58 to 1.16, 1.16 to 1.74 and 1.74 to 2.32 microns, the amounts are respectively 4.53 per cent. per micron, 3.08 per cent. per micron, and 4.71 per cent. per micron. Less striking, but equally obvious figures are found in other parts of the paper by Dr. Work. It must be noted in this connection that the range below 0.58 micron corresponds to that in which the resolving power of microscopes disappears because the wave length of light is too large for the objects under inspection. Dr. Work himself says that 0.25 micron is the minimum size that can be detected under the microscope (p. 24). Furthermore, it is likely that this restriction (0.25 micron) is not a rigid one. Since grains generally lie on the microscope slide with their smallest dimension at right angles to it, and the dimension determined by Work corresponds to some intermediate value between the largest and the intermediate diameter (p. 19), it is quite possible that the majority of grains just smaller than 0.5 micron (as measured by Work) are invisible because of thinness, or small intermediate dimension.

It should be considered, as was rightly done by Work, that "the count in the lowest size range may be low, as the limits of visibility were close" (0.59). Unless otherwise supported by experimental evidence, it would seem proper, therefore, to consider that unsized pulverized materials do contain grains finer than 0.5 micron, including grains fine enough to approach unit crystals.

E. A. Hersam, Berkeley, Calif. (written discussion).—These papers on crushing and grinding fulfill a demand of milling to confirm a fundamental principle, the confusion of which, for a long time, has retarded advancement of the development of efficiency in crushing. It has been recognized for a long time that crushing is essentially the act of producing new surface by rupture. It has been shown that the measurement of crushing is the measurement of new surface,[5] counting as energy lost all that which is expended without producing new surface. No research before has shown this relationship between energy and surface so convincingly, nor have observations been secured under conditions so carefully controlled and measured. Surface measurement by screening has been too rough to furnish the precision exacted. From now on, it becomes possible to develop standards of efficiency that have lain in wait for the costly and enterprising piece of research that this is seen to be. With this accomplished, the most appealing part of the progress can begin. Costs thus far in experience and experimentation are as nothing compared with the economies that can come to industry. Great practices, in which crushing, grinding and pulverizing are the items of major expense, are multiplying rapidly under the new requirements and in the light of newly discovered possibilities. Such developments will appear in increasing succession not only in lixiviation but in flotation, in cement manufacture and in many branches of milling. The practice of tomorrow can be appraised on a basis that is now reclaimed from the region of dispute.

F. Tartaron, Clarkdale, Ariz. (written discussion).—In the methods of verification of the solution process of determining surface, the authors have not, in the opinion of the writer, proved their case absolutely. The evidence given supports their conclusions with a high degree of probability, but lacks scientific rigidity. The writer, however, does not wish to argue this, but would much rather present a method, which, he believes, proves or disproves absolutely their basic assumption—*i. e.*, Wenzel's law—that the reaction velocity between a solid and a liquid is proportional to the area of contact. The difficulty with Wenzel's law is that nothing has been said concerning a possible change in rate of solution with change in size of particle. Small spherical

[5] E. A. Hersam: Measurement of the Work in Crushing. *Jnl.* Franklin Inst. (1923) **196**, 95–104.

particles have greater curvature than larger spherical particles. For cubes, there is a marked increase in the ratio of edge length to area with decreasing size of particle. Since an edge may be considered as a place of abrupt curvature, we have with cubes the same condition as with spheres, that is, increasing curvature with decreasing size. It is possible that rate of solution is not only a function of quantity of surface but also of curvature of surface.

The following method appears satisfactory for settling this point. Assume two particles $A$ and $B$ placed in contact with the same reacting liquid at the same time. Particle $B$ is smaller than $A$, hence has less surface. Suppose that surface $A$ is twice as great as surface $B$ the instant they come in contact with the liquid. Let us now consider a surface layer one molecule deep on each particle (as indicated by the dotted lines). Since $A$ has twice as much surface as $B$, there are twice as many molecules in the $A$ layer as in the $B$ layer. But since, according to Wenzel's law, the quantity dissolving at any instant is directly proportional to surface, the $A$ layer will be removed *in the same interval of time* as the $B$ layer. Two new surfaces are now produced which stand in a different ratio. To be concrete, let us assume this ratio to be 2.1/1. But now the rates of solution will adjust themselves in the same ratio. Thus the new molecular layer on particle $A$ will have 2.1 times as many molecules as the new molecular layer on $B$ but the $A$ layer will dissolve 2.1 times as fast. This indicates that equal reductions in size take place in equal intervals of time, if Wenzel's law is unaffected by difference in size.

FIG. 5.

Now let us take a single particle in contact with the reacting liquid. The surface molecular layer will dissolve in a certain interval of time, leaving a smaller particle with less surface. The rate of solution, however, will always adjust itself to the new surface so that each molecular layer is dissolved off in the same interval of time. Hence, we reach the conclusion that there is a straight-line relation between the diameter of a particle dissolving in a liquid and the time of solution, expressed as follows:

$$-D = kT$$

the minus sign being used because $D$ decreases as $T$ increases.

The two interfering factors of internal surface and change in concentration of solution can be easily minimized; the first by using Ottawa sand, the second by taking a large enough bulk of liquid with respect to the quantity of quartz, so that the change in concentration becomes negligible. The figures in the first paper show that for the usual case, in which 25 c.c. of the standard HF solution were used and 50 mg. of quartz dissolved in 2 hr., the change in concentration is approximately 3.5 per cent. By using 250 c.c. of standard HF solution (which the authors used in some cases) this change in concentration can be reduced to 0.35 per cent., which certainly is negligible.

We can, therefore, take the relation, $-D = kT$ as experimentally realizable as well as theoretically true. We know that

$$\text{Surface} = k'D^2$$

hence by using this and the preceding relation we get:

$$S = -(k''T^2)$$

Now taking the logarithm of each side, we have

$$\log S = -(\log k'' + 2 \log T)$$

Thus, we have a straight-line relation between the logarithm of surface and the logarithm of time. We can measure time accurately, the equation is true if Wenzel's law is true, hence the measurements of surface must check this relation.

Another extremely simple method, but involving the unverified assumption made by Gross and Zimmerley that the true average size of particles between two screen sizes is the arithmetical average of the screen sizes, is as follows: Surface $= kD^2$. Taking logarithms of both sides, we have:

$$\log S = \log k + 2 \log D$$

Hence there is a straight-line relation between the logarithm of surface and that of diameter. This, of course, applies only to Ottawa sand, having no internal surface. Referring to the graph given on page 31 of the second paper, we find that this relation is realized. This is another piece of evidence in favor of the method, but it is not scientifically rigid (though extremely probable), because it is based on the unverified assumption that for the sizes taken, screen averages give the true average diameter of the particles.

J. Gross and S. R. Zimmerley (written discussion).—Mr. Tartaron's discussion brings up some interesting points that have also been noted by Professor Taggart in his comments on the extremely fine material, although perhaps from a different angle.

The change in specific dissolution rate of particles in which the percentage of edge and corner atoms becomes appreciable has been taken up in the reply to Professor Taggart's discussion (p. 22). The calculations given show that for a cube 0.01 micron in size only 5 per cent. of the atoms are more active on account of edge positions. This size is far beyond microscopic visibility and to maintain a proper perspective we should remember that the limit of surface calculations, in previous attempts to verify Rittinger's law, has been the 200-mesh particles, which have a diameter 7400 times that of the limiting one discussed.

Mr. Tartaron has given an expression which states that a straight-line relation exists between the logarithm of surface and logarithm of time. At one time, we considered a method of surface measurement based on the time required to dissolve a definite amount of silica. This could be done by interpolation on a cumulative curve. Such a method, however, would require the determination of $K$, the accuracy of which would depend on surface determinations. It is true that a straight-line relation exists between the logarithm of surface and the logarithm of time as long as no change of surface takes place; this change of surface may be ignored with coarse material but with fine material the change in surface may be very great, hence the change in rate of dissolution may be great. As the determination of the initial rate is dependent on this change of rate, we felt that the I. R. value would give a more accurate surface figure.

Mr. Tartaron also points out the relationship between size of particle and surface and the possibility of a method of surface measurement based on this relationship. Such a method would ignore interior surface and would involve the measurement of particles, an impossibility with fine particles.

The excellent understanding of the problem as shown by Professor Gaudin's discussion makes his support of the work in general a matter of considerable satisfaction to the authors. The difference in the estimates of Gaudin and ourselves on the 200-mesh material mentioned may be due in part to the failure of the extrapolation to completely compensate for a more rapid dissolution of the very fine particles during the first minutes of the test. It should be pointed out that this could only apply to the finest grade separated, −200 or 400 mesh from sieve sizing, or to finest elutriation product.

Professor Gaudin suggests the use of a larger amount of solution or a more dilute solution for the dissolution of the finest product. The use of a larger quantity of solution brings in experimental difficulties but the results give a flatter curve more easily extrapolated. The use of more dilute solutions also gives a flatter curve. The

use of as large a quantity of dilute solution as possible for fine material would probably give more reliable results. Some experiments made on surface measurements of −400-mesh quartz indicate that with increased quantity of solution the surface measurements are slightly greater, and that with more dilute solutions the surface measurements are also greater. These experiments were not sufficiently satisfactory for publication and need verification; they point out that Gaudin's contention may be correct, but to what extent we are as yet unable to say. The results indicate, however, that the increased surface measurements thus obtained would not be sufficient to change our average size of 5 microns to 2, as obtained by Gaudin.

While we realize that our extrapolation on very fine material is possibly too low, it may also be possible that Gaudin's extrapolation is too high and that the true average of size lies somewhere between.

As pointed out by Professor Hersam, the work so far consists in the preparation of a foundation for the study of crushing and grinding efficiencies. In the study of grinding efficiencies it is necessary to know two things: the work put into the operation and the work represented by the product.

We have a small ball mill equipped with an integrating power-reading device, adapted from one used by Prof. H. E. T. Haultain, which measures the power at the the mill, approximately 95 per cent. of which goes to the balls. This gives rather accurately the work going into the operation. The surface measurement of the product gives the work represented by the product. From these two factors we get efficiencies. This work is now in progress.

# A Laboratory Investigation of Ball Milling*

By A. M. Gow,† A. B. Campbell‡ and Will H. Coghill,§ Rolla, Mo.

(San Francisco Meeting, October, 1929)

The trend in ball milling has been toward mills of larger diameter, but without fundamental laws as a guide. The speeds at which mills are run have been a matter of cut-and-try. This paper deals with both diameter and speed and proposes to show the laws which apply to some laboratory ball mills, ranging in diameter from 18 to 42 in., run at various speeds. The correlation of power, speed and grinding rate of the respective mills will be shown by curves of markedly significant similarity. Before presenting the results some consideration will be given to the mechanics of ball milling.

## Mechanics and Theory of Ball Milling

As early as 1904, Herman Fischer[1] reported observations on specially constructed ball mills which allowed the paths of balls to be studied. The following conclusions were drawn:

1. Balls do not grind the ore, but crush it by impact.
2. At slow speeds the balls roll down the inclined heap, but at higher speeds the balls close to the wall adhere to it until they reach a certain height, whence they are thrown through an arc to the bottom.
3. The falling balls do not come down in clusters, but in series, the balls of each row keeping to their own line of flight according to their distances from the wall while ascending.
4. A further increase in speed results in the balls adhering during the whole of the circuit to the side of the drum. (This centrifuging speed may be called the "critical" speed and may be taken as a reference basis, since it is a constant function of the diameter.)[2]

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[1] H. Fischer: Der Arbeitsvorgang in Kugelmuhlen, insbesondre in Rohrmühlen. *Ztsch.* Ver. Deut. Ing. (1904) **48**, 437.

[2] Numerically the critical or centrifuging speed is equal, in revolutions per minute, to 54.19 divided by the square root of the radius in feet.

5. "The line of flight may be computed for each ball. The vertical force of the movement is reduced until the ball reaches the apex. Of course, a reduction of speed in the direction of the line of flight results, and the balls approach each other at the apex, and at the same time influence each other's flight. But if we omit this disturbance, we shall see the ball continue in its flight and the distance between it and its followers increase." See Fig. 1.

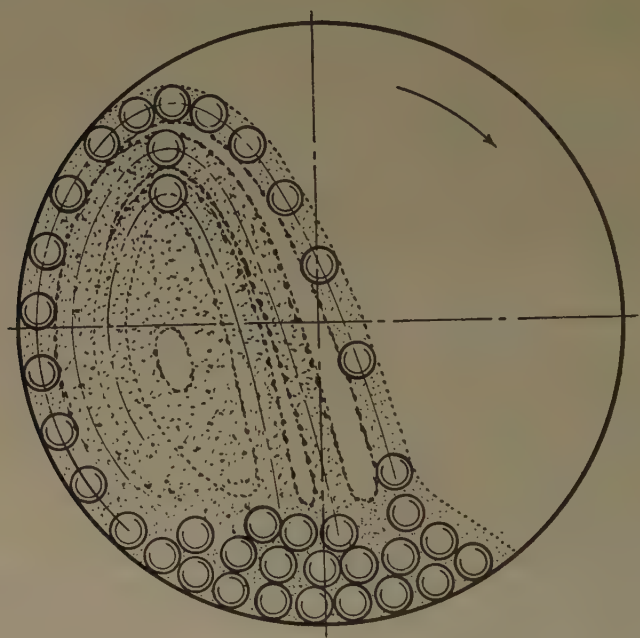


FIG. 1.—ACTION OF BALLS IN TUBE MILL ACCORDING TO HERMAN FISCHER.

6. The speed, which was recommended as correct, is between 76 and 83 per cent. of the critical.

The following year, 1905, H. A. White[3] read a paper on the theory of the tube mill. In this he discussed ball paths and gave mathematical reasoning. He calculated ball paths as though they were parabolas of free-falling bodies. His paper was illustrated with photographs of small glass-covered mills. He suggested operating a mill at the critical speed so that the centrifuged balls could act as a liner.

In 1919, E. W. Davis[4] presented an exhaustive mathematical discussion of the mechanics of ball milling. He reasoned that after the balls leave their circular paths they follow the parabolic trajectories. Based

[3] H. A. White: The Theory of the Tube Mill. *Jnl.* Chem. Met. & Min. Soc. of South Africa (1905) **5**, 290.

[4] E. W. Davis: Fine Grinding in Ball Mills. *Trans.* A. I. M. E. (1919) **61**, 250.

upon this assumption, Davis calculated the ball paths and recommended a speed of about 75 per cent. of the critical, provided there was no slippage. He stated that horsepower, for the most efficient operating speed, is proportional to the 3/2 power of the radius.

Fischer regarded the balls, after leaving their circular paths, as having a retarded velocity on their upward flight. The mathematics of White and Davis accept this idea. Fischer's diagnosis was not complete, and as a result it has been supposed that the balls are thrown a shorter distance than is actually the case; hence operators have been influenced to run their mills too fast. The relation of power to mill radius as given by Davis will be treated in its turn.

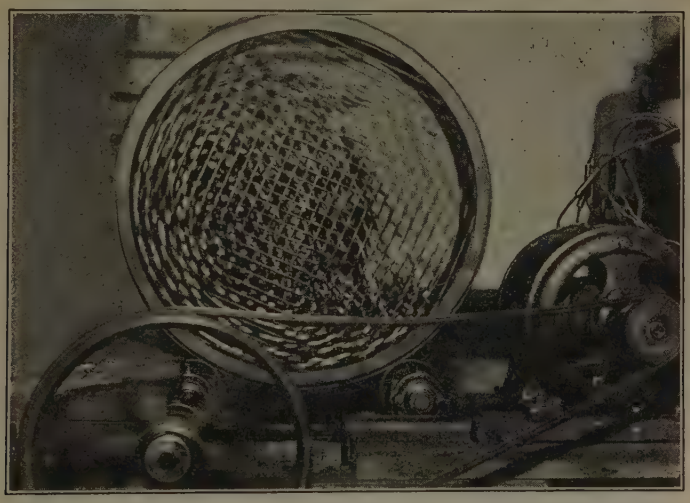


FIG. 2.—THREE-FOOT SQUIRREL-CAGE MILL SET-UP IN ACTION.

The early writers were aware that balls roll down the heap when the mill is run slowly, and are thrown through the air when the mill is run fast. The term "cascade" may be applied to the former deportment and "cataract" to the latter; these terms are strictly in accord with the dictionary and are needed in ball milling literature.

Thus in the previous investigations the assumption has been made that the rising balls behave like projectiles when they are thrown across the mill. This assumption seems erroneous.

In order to record and study ball paths, a ball mill 3 ft. in diameter by 6 in. long was equipped with wire screen ends of 1-in. mesh. It was placed, when properly loaded, on motor-driven rolls, which could be revolved at any desired speed. Traces, sketches and photographs were made of the balls in action at various speeds and under different loads. Iron balls of 1¼-in. dia. were used, and the mill was operated dry; that is,

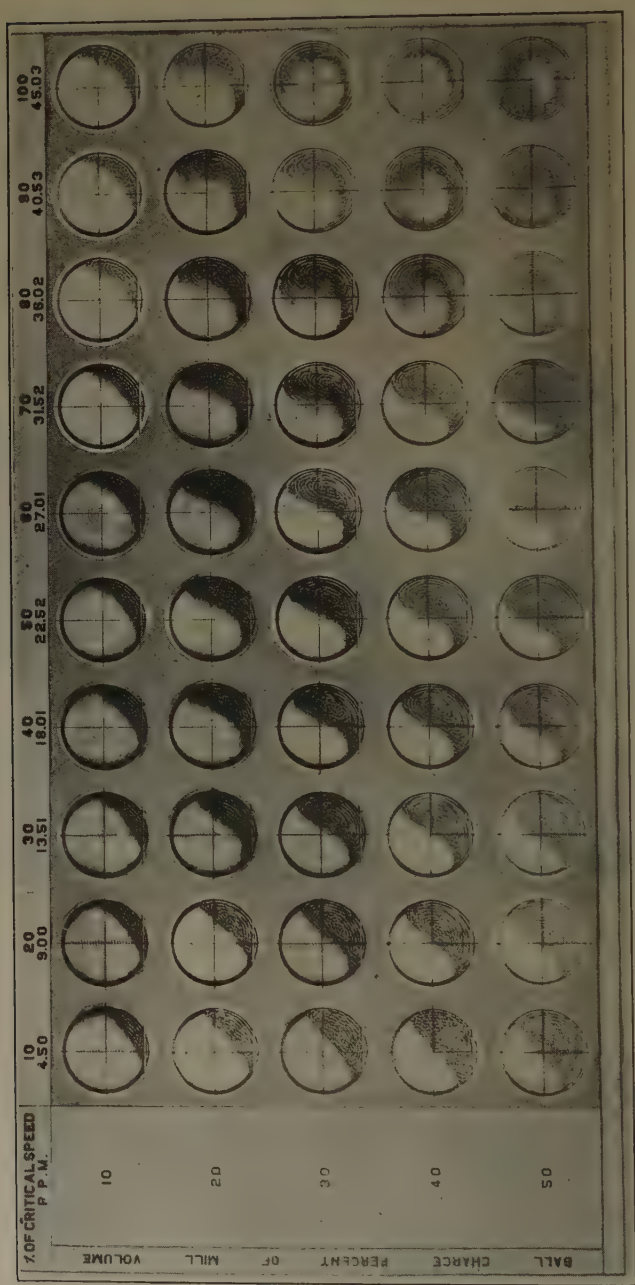



FIG. 3.—THREE-FOOT SQUIRREL-CAGE MILL OPERATING AT VARIOUS LOADS AND SPEEDS.

with balls alone. This "squirrel-cage" mill is shown in Fig. 2, and the action photographs in Fig. 3.

When a ball charge equivalent to 10 per cent. of the mill volume is rotated in the squirrel cage, the balls, as they are lifted to the top, cascade or roll down the side of the mass. The faster the mill revolves, the faster the balls are lifted to the top, but slippage is so great that none of the balls attain a speed great enough to be thrown into space. They do not cataract. At the predetermined critical speed none of the balls are carried over, or centrifuged, as implied by the term "critical."

With a ball load of 20 per cent. of the mill volume, some of the balls are thrown into the air at the higher speeds, but slippage still prevents their being centrifuged at the critical speed. The balls that are thrown at the higher speeds fall upon a toe of balls at the bottom of the heap and do not hit the liner of the mill.

When the ball charge is increased to 30 per cent. of the mill volume this toe is better developed. At the higher speeds the outside balls are thrown beyond the toe and strike the lining. Although they do rise well up toward the top of the mill at the critical speed, they still fail to maintain contact with the lining. A slight amount of slippage prevents the ball charge from attaining the mill speed.

Slippage, or relative motion between the charge and the shell, is overcome with some ball charge between 30 and 40 per cent. of the mill volume, as is evidenced by the fact that the latter loading causes the outermost balls to centrifuge at the critical speed. During the test no slippage could be observed at the slower speeds at this loading. The toe is very prominent and receives the blows of falling balls at speeds up to about 75 per cent. of the critical.

A load of 50 per cent. of the mill volume gave ball paths similar to the former ones, but the swelling of the charge results in crowding, which is shown by the longer trajectories. These observations are recorded in photographs shown in Fig. 3 and in sketches, made by tracing the paths of the outermost series of balls on an adjacent glass plate, as shown in Fig. 4.

The squirrel-cage observations show that balls are thrown farther than is hypothecated by the old parabolic path theory. This is best shown by a photograph, Fig. 5. The inner superimposed curve represents the ball path according to old theories; the outer one, the path by the new theory to be discussed. Because of its magnitude the difference requires critical examination.

The fallacy of the old parabolic theory lies in the fact that the balls do not act independently when they leave the shell, but continue in contact, pushing those ahead, until they pass the apex of their flight. The continuous upward stream of balls can not lose velocity and consequently there is a horizontal velocity at the apex of their flight equal

to the peripheral velocity of their circular course. From this point they are free-falling except as they are hindered by atmospheric friction, crowding and impact.

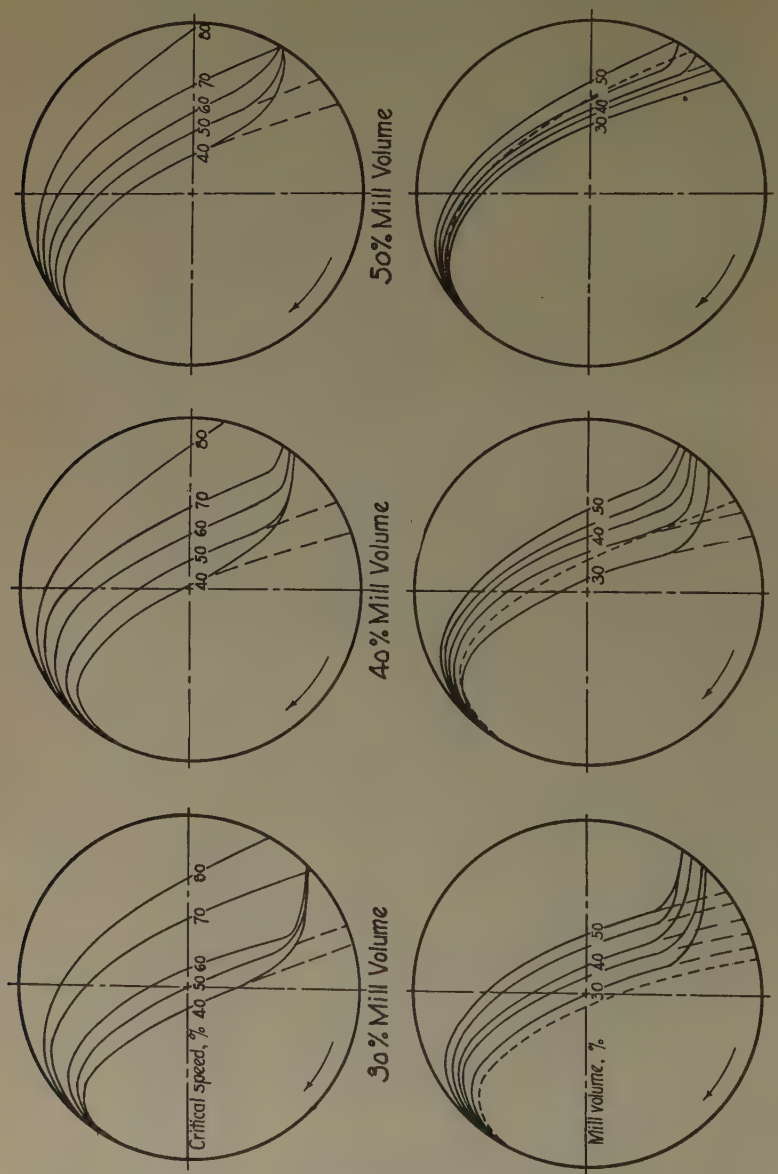



FIG. 4.—OUTER PATHS OF BALLS IN 3-FT. SQUIRREL-CAGE MILL AT VARIOUS LOADS AND SPEEDS. Dotted lines in lower diagrams represent theoretical paths according to the new formulas.

Substantiating experiments were made. These showed that when a succession of several balls is projected upward, the first of the series goes farther than a single ball shot at the same angle and velocity.

Fischer recognized this pushing effect with the remark that the balls influence each other's flight, but he failed to consider it in his computations.

## Derivation of the New Equation

The equation of the path of such a pushed body has been worked out by G. R. Dean[5] in collaboration with R. L. Kidd[6] and is found as follows:

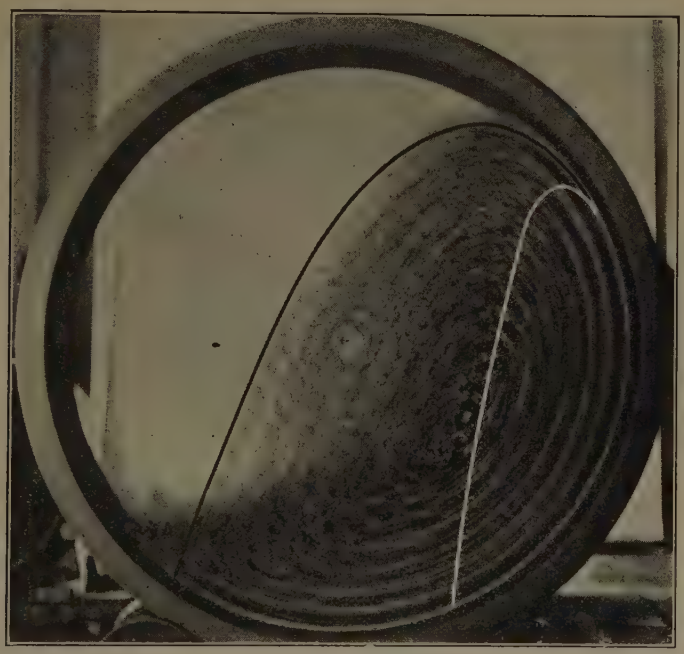


Fig. 5.—Comparison of actual path of outside layer of balls with their theoretical paths as determined by old formula (white line) and by new formula (black line). The mill is revolving at 60 per cent. critical speed.

To find the equation of the ball path, in a vertical plane, followed by a particle whose velocity along the path is constant and whose direction of travel is affected by gravity (Fig. 6):

Velocity along curve is constant $= V$,

Mass of particle $= M$,

Radius of curvature $= \rho$,

Normal acceleration $= \dfrac{V^2}{\rho}$,

Force acting outward, normal to curve $= \dfrac{MV^2}{\rho}$,

[5] G. R. Dean, Professor of Mathematics, Missouri School of Mines and Metallurgy.

[6] R. L. Kidd, Research Fellow, Missouri School of Mines and Metallurgy, 1928–29.

Force acting inward, normal to curve $= -Mg \cos \beta$.

These two forces must be equal, therefore: $\frac{MV^2}{\rho} = -Mg \cos \beta$,

or

$$\rho \cos \beta = -\frac{V^2}{g} \qquad [1]$$

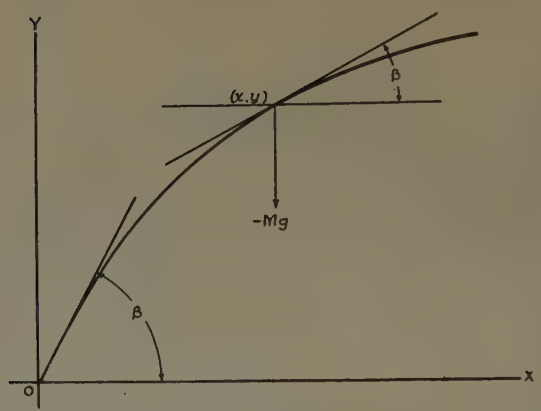



FIG. 6.—BALL PATH FROM SHELL TO TOP OF ITS FLIGHT.

The equation for the radius of curvature is:

$$\rho = \frac{\left[1 + \left(\frac{\delta y}{\delta x}\right)^2\right]^{3/2}}{\frac{\delta^2 y}{\delta x^2}}$$

since $\cos \beta = \frac{\delta x}{\delta s} = \frac{1}{\left[1 + \left(\frac{\delta y}{\delta x}\right)^2\right]^{1/2}}$

The last statement is true since $\frac{\delta s}{\delta x} = \left[1 + \left(\frac{\delta y}{\delta x}\right)^2\right]^{1/2}$

Substituting these values in equation 1 we have:

$$\left[\frac{\left[1 + \left(\frac{\delta y}{\delta x}\right)^2\right]^{3/2}}{\frac{\delta^2 y}{\delta x^2}}\right]\left[\frac{1}{\left[1 + \left(\frac{\delta y}{\delta x}\right)^2\right]^{1/2}}\right] = -\frac{V^2}{g}$$

Simplifying,

$$\frac{1 + \left(\frac{\delta y}{\delta x}\right)^2}{\frac{\delta^2 y}{\delta x^2}} = -\frac{V^2}{g} \qquad [2]$$

or
$$\frac{\dfrac{\delta^2 y}{\delta x^2}}{1+\left(\dfrac{\delta y}{\delta x}\right)^2} = -\frac{g}{V^2} \qquad [2a]$$

Integrating, $\tan^{-1}\dfrac{\delta y}{\delta x} = -\dfrac{gx}{V^2} + C$

In the above equation, $\dfrac{gx}{V^2}$ must be expressed in degrees, so multiplying by 57.29 we have:

$$\tan^{-1}\frac{\delta y}{\delta x} = -57.29\,\frac{gx}{V^2} + C,$$

or
$$\frac{\delta y}{\delta x} = \tan\left[-57.29\,\frac{gx}{V^2} + C\right] \qquad [3]$$

When $x = 0$, $y = 0$, and $\dfrac{\delta y}{\delta x} = \tan\beta$

Hence: $C = \beta$

Then equation 3 becomes:

$$\frac{\delta y}{\delta x} = \tan\left[\beta - 57.29\,\frac{gx}{V^2}\right] \qquad [3a]$$

or
$$\delta y = \tan\left[\beta - 57.29\,\frac{gx}{V^2}\right]\delta x$$

$$y = \int \tan\left[\beta - 57.29\,\frac{gx}{V^2}\right]\delta x$$

$$= \frac{V^2}{g}\log_e\cos\left(\beta - 57.29\,\frac{gx}{V^2}\right) + C'$$

When $x = 0$, $y = 0$, and $C' = \dfrac{-V^2}{g}\log_e\cos\beta$. Then we have:

$$y = \frac{V^2}{g}\left[\log_e\cos\left(\beta - 57.29\,\frac{gx}{V^2}\right) - \log_e\cos\beta\right] \qquad [4]$$

Equation 4 is for balls of infinitesimal size. Changing equation 4 from the base $e$ to the base 10, we have:

$$y = 2.3025\,\frac{V^2}{g}\left[\log_{10}\cos\left(\beta - 57.29\,\frac{gx}{V^2}\right) - \log_{10}\cos\beta\right] \qquad [4a]$$

or
$$y = 2.3025\,\frac{V^2}{g}\left[\log_{10}\left(\frac{\cos\left(\beta - 57.29\,\dfrac{gx}{V^2}\right)}{\cos\beta}\right)\right] \qquad [5]$$

The highest point in the curve is where $\dfrac{\delta y}{\delta x} = 0$. Substituting in equation 3$a$, we have:

$x = \dfrac{V^2\beta}{g}$, where $\beta$ is expressed in radians. [5$a$]

Then $y_{max} = 2.3025\,\dfrac{V^2}{g}\log_{10}\sec\beta$ [5$b$]

## Ball Action in Squirrel-cage Mill

By the use of this equation 5, ball paths at various speeds may be drawn as in Fig. 7. The solid lines represent the new equation and the dotted lines the old one. When these new curves are compared with the observed photographs and sketches they are seen to resemble closely the actual paths described in the mill containing just enough balls to prevent slippage. This close resemblance is shown by noting the outer superimposed curve in Fig. 5 and the dotted lines in the lower row of Fig. 4.

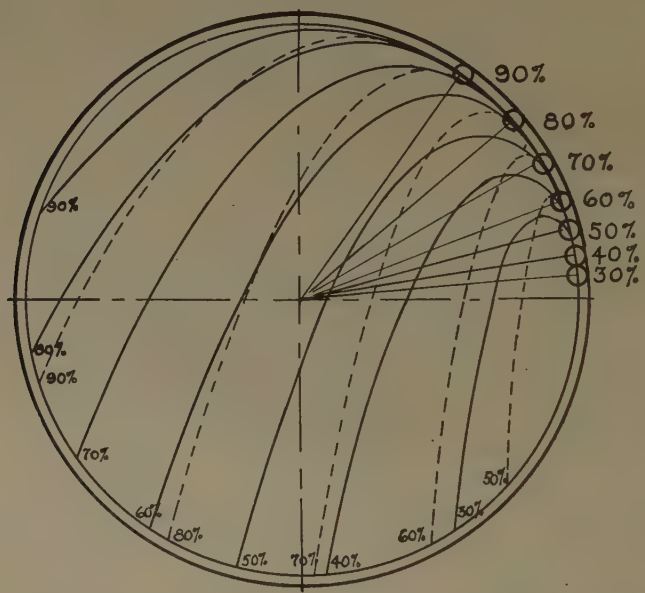



Fig. 7.—Outside layer ball path at various speeds according to old parabolic formula and new formula (solid lines).

As has been pointed out above, and as shown in Fig. 4, an increase in ball load causes crowding and throws the balls outward. When the mill is loaded so that there are many layers of balls, concentric with the shell, there is not enough room under the normal trajectory of the outer layer to permit the underlying layers to take their normal courses. Consequently, a crowding occurs, which causes a slight distortion in the ball paths. The normal paths of the several layers are shown in Fig. 8. The impossible overlapping of the inner balls illustrates this crowding.

Having determined the action of balls in the squirrel-cage type of mill, the question arose as to whether the addition of ore and water affects the behavior of the grinding media. Previous experimenters have stated that the addition of pulp causes slip, with the result that the

effective speed is less than the mill speed. Records of power required to operate the squirrel-cage mill are very similar to those of a ball mill of the same size. The ball mill tests will be discussed later, but the power-speed curves indicate that for similar loading of the squirrel cage and the ball mill the power peaks are at about the same speeds in each case. The similarity of the curves in Fig. 9 indicates that no great difference exists between the behavior of the squirrel-cage mill and that of the similar ball mill with pulp charge.

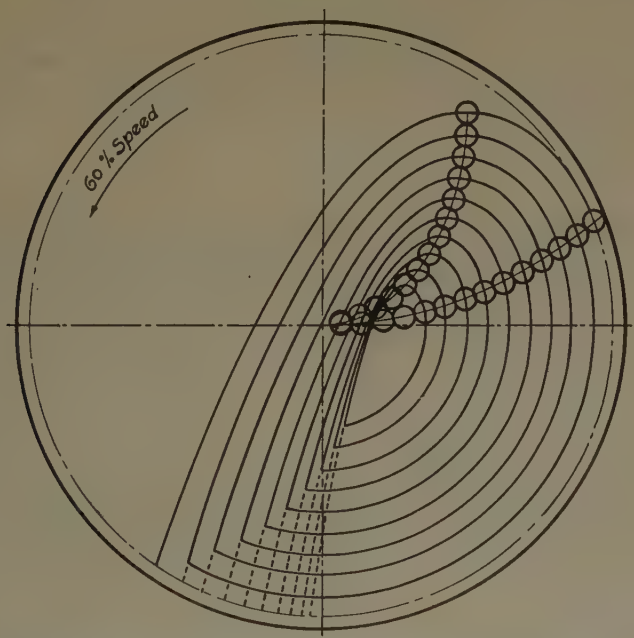



FIG. 8.—PATHS OF CONCENTRIC LAYERS OF BALLS WHEN MILL IS ROTATING AT 60 PER CENT. OF CRITICAL SPEED ACCORDING TO NEW THEORY.

When a mixture of large and small balls was tumbled in the squirrel cage, a segregation resulted, depending on the speed. At slow speeds the large balls often rolled out ahead of the toe and remained there for short intervals. The tendency was for them to go to the outside of the ball charge, but when the speed was sufficient to cause a void in the center of the mass, the larger balls concentrated in the vacant area. This phenomenon is a function of size. Large wooden and large iron balls behaved in the same way.

This segregation by size occurs because the center of mass of a small ball can be closer to the mill shell than the center of mass of a larger one. Small balls thus may be cataracted from a longer radius and hence have a greater speed with respect to the critical than a large ball which is on a shorter radius. Consequently the small ball can be carried farther up the

mill shell and be cataracted so as to be in the outside layer in a succeeding cycle. Because of its slower speed the large ball falls short and is forced into one of the inner layers. The result is that large balls are forced to the central open area where they avoid the buffeting and crowding of the smaller ones. This argument does not apply where the mill is run so slowly that cataracting does not occur.

Ore particles, which are still smaller than balls, would be expected to exhibit the same tendency of outward migration; a layer of small ore particles may be considered to line the mills and partly protect the linings from the numerous blows of the small balls. When balls wear to such a size that they possess no longer the kinetic energy necessary to crack the ore particles, they reduce milling efficiency by occupying valuable space.

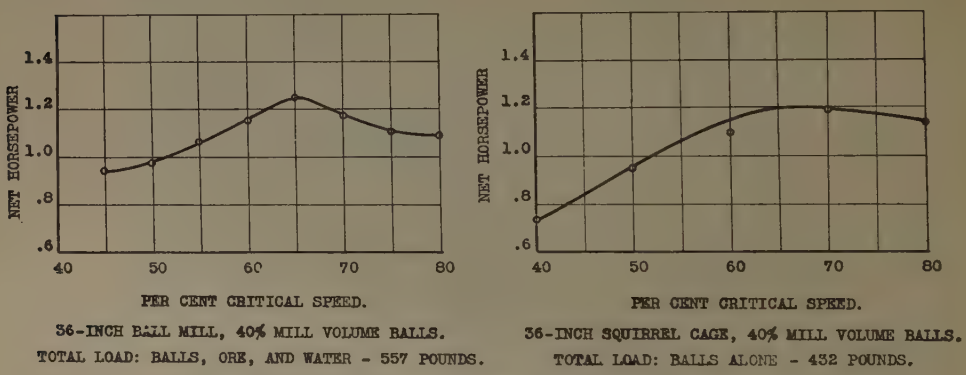



FIG. 9.—COMPARISON OF POWER REQUIRED BY BALL MILL AND SQUIRREL CAGE.

Observations of the ball action in the 3-ft. by 6-in. squirrel-cage mill follow:

1. Slippage was minimized by the use of a short mill and small balls. It was a function of the amount of the charge. It became negligible when the charge was more than about 35 per cent. of the mill volume.

2. When the charge is about 40 per cent. of the mill volume and the speed is below 75 per cent. of the critical, a toe is formed at the bottom of the heap which prevents the balls from hitting directly on the lining.

3. The balls did not follow a parabolic path when thrown from the circular path of the mill shell. They followed a course that was longer, and went a greater distance across the mill.

4. Increasing the ball charge beyond 40 per cent. of the mill volume resulted in crowding which caused the balls to take a still longer path.

5. When a ball charge of mixed sizes was run at a cataracting speed the small balls segregated on the outer paths where impact is greatest. Their small diameters permitted their center of mass to lie close to the shell where the centrifugal force was maximum.

6. On account of the longer paths, slower speeds gave the same results as were hypothecated by the higher speeds required by the old parabolic path theory. Where a speed of 75 per cent. of the critical had been recommended to give the maximum ball energy, a speed of 50 to 65 per cent. was advisable.

This last deduction was substantiated by the results of several series of grinding tests made to determine the operating characteristics of the ball mills. A discussion of these follows.

## Grinding Tests

The operating characteristics of the ball mills were studied by making grinding tests under predetermined conditions. Five mills of construction similar to that of the squirrel cage, but with solid ends, were employed. They were 18, 24, 30, 36 and 42 in. dia., respectively, and

Fig. 10.—Five laboratory ball mills with 3-ft. mill arranged as squirrel cage.

each was 6 in. long. They are shown in Fig. 10. They were designed for batch grinding and made of short length to minimize slippage. The 42-in. mill, however, was equipped with special feed and discharge trunnions so that it could be run continuously when desired. When it was run as a continuous mill, an automatic feed was used with it. These appear in Fig. 11. All the mills were of the tire-and-roller type. The rollers were adjustable for the various mills and were electrically driven by a direct-current motor. The set-up is shown in Fig. 12. Electric meters were used to obtain power data.

Iron balls of 1¼-in. dia. were used. The material ground was flint tailings from the Tri-State zinc district, roll-crushed through 3/16-in. and retained on 1-mm. screens.

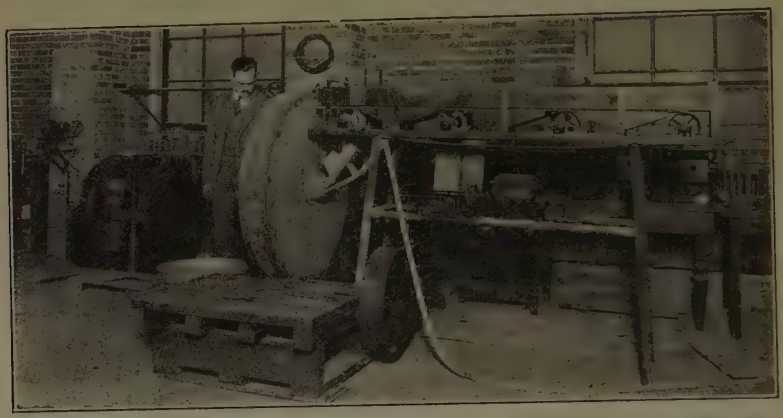


Fig. 11.—Forty-two inch mill with feeder set-up for continuous grinding.

Fig. 12.—Ball mill set-up for grinding tests.

*Procedure*

Each test consisted of placing a charge of ore, balls and water in a mill, bolting on the cover and rotating the mill at a predetermined speed for a short time. During the grinding period electrical readings were taken and from these the power consumption was subsequently calculated. Upon completion of the grinding period the mill was opened, the charge removed, and the pulp washed from the balls. Samples of the original feed and of the ground pulp were screened in the standard sieves. From

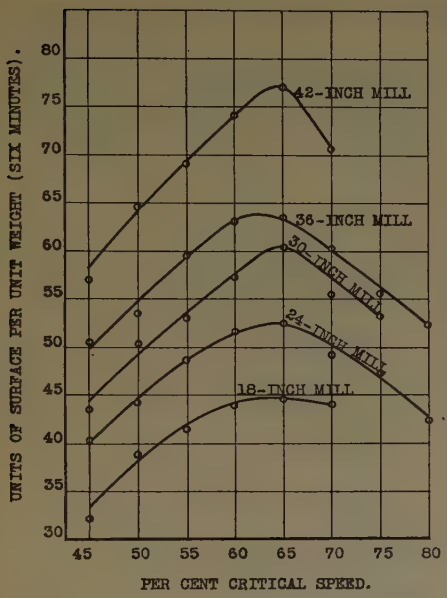



FIG. 13.—GRINDING RATE PER UNIT WEIGHT.

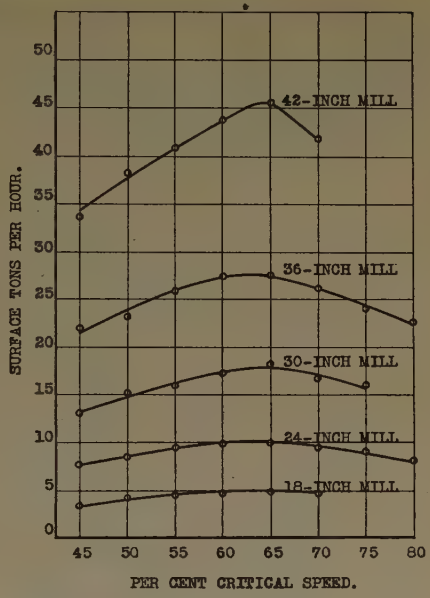



FIG. 14.—OVER-ALL GRINDING RATE.

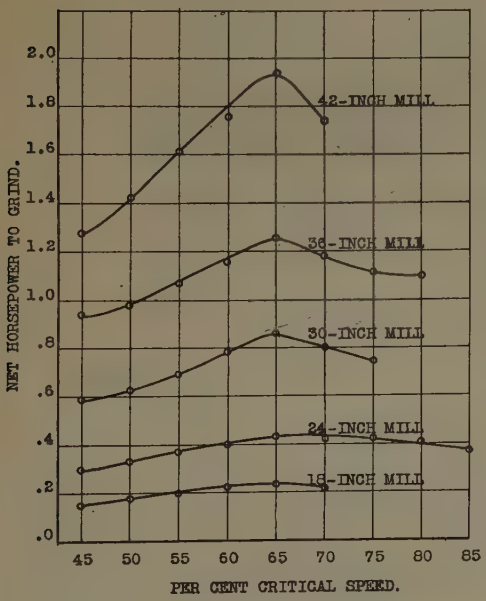



FIG. 15.—POWER CONSUMPTION IN GRINDING.

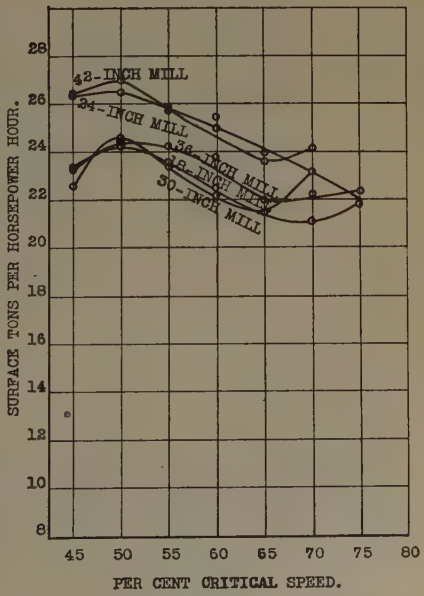



FIG. 16.—EFFICIENCY IN GRINDING.

these sizing analyses the units of surface were calculated by a previously discussed method.[7] Crushing is a surface-producing process. The difference in the surface units in the discharge and the feed represent the amount of new surface made by crushing. It has been proved by

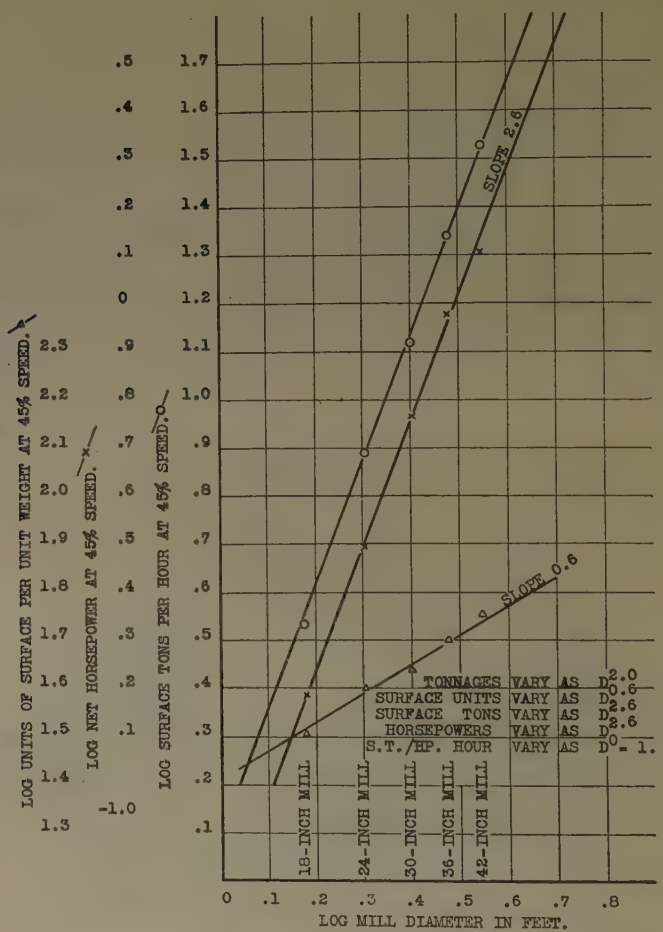



FIG. 17.—GRINDING CHARACTERISTICS AT 45 PER CENT. CRITICAL SPEED.

Gross and Zimmerley[8] that the work involved is proportional to the new surface created. The units of surface produced multiplied by the tonnage handled by the mill in one hour of grinding time give the surface tons per hour, or the grinding capacity of the mill. This figure when divided by

[7] W. H. Coghill: Evaluating Grinding Efficiency by Graphical Methods. *Eng. & Min. Jnl.* (1928) **126**, 934.

[8] J. Gross and S. R. Zimmerley: Crushing and Grinding—III. Relation of Work Input to Surface Produced in Crushing Quartz. See page 35.

the horsepower gives surface tons per horsepower-hour, or the grinding efficiency of the mill.

The determination of power was made from the electrical data and motor characteristics. The entire motor output does not go into crushing. Some of the power rotates the mill, overcomes friction and accom-

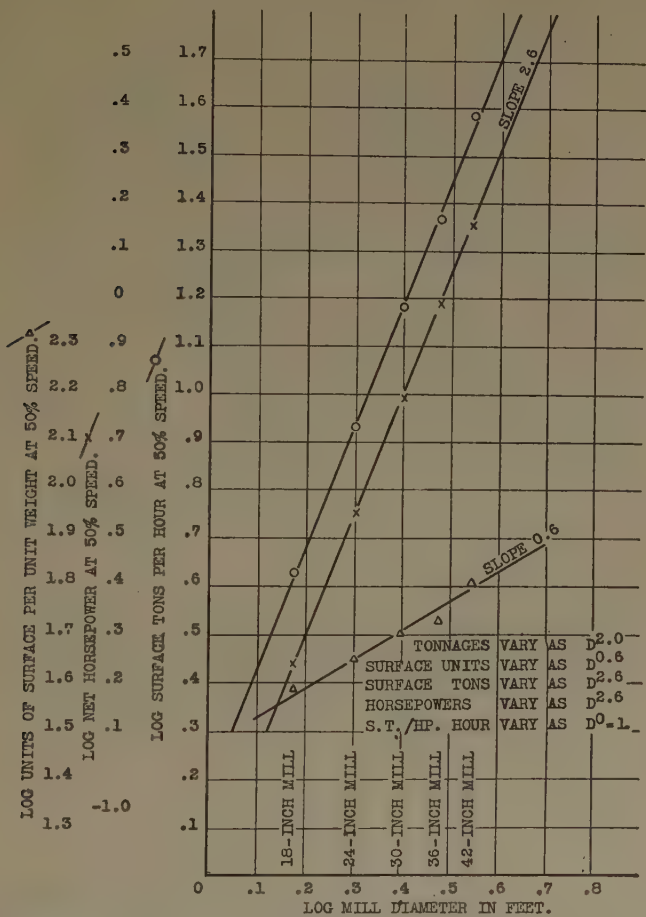



FIG. 18.—GRINDING CHARACTERISTICS AT 50 PER CENT. CRITICAL SPEED.

plishes other work which should not be charged against comminution. This constitutes the dead load, and had to be determined for the various mills. Each one was loaded concentrically with a weight equal to that of the charge, and rotated as a flywheel at the various speeds. The net power was calculated in each case. This dead load was subtracted from the gross to determine the net power to grind. Thus all the power data apply solely to the energy spent within the shell of the mill and in this

way are not comparable with the power readings commonly made in the plants.

Batch grinding tests were made with the five mills, each at various speeds. Time of grinding was 6 min. This period was chosen as being of suitable duration to allow power readings to be taken and yet short enough to avoid an excessive production of slime.

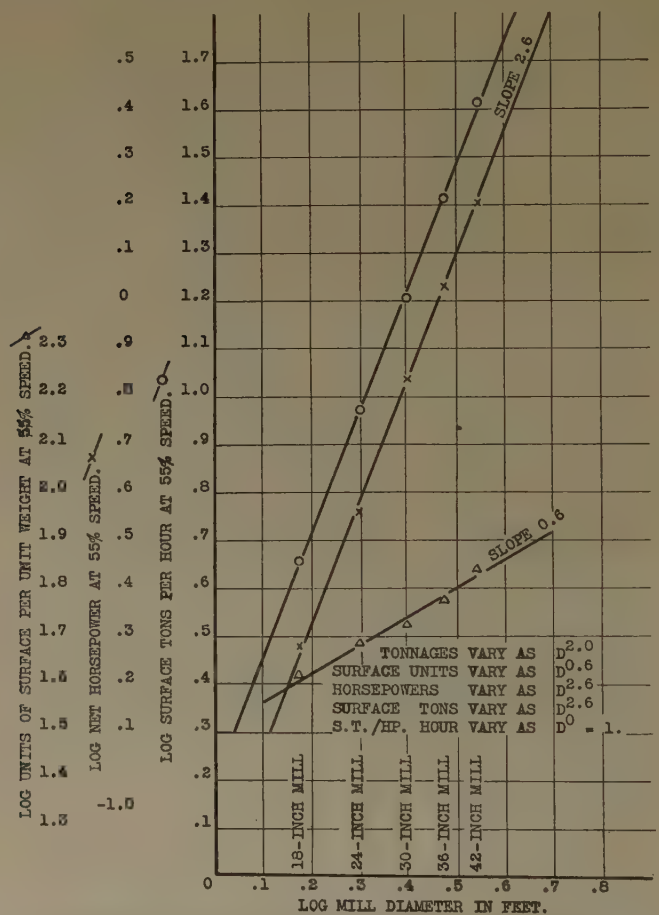



FIG. 19.—GRINDING CHARACTERISTICS AT 55 PER CENT. CRITICAL SPEED.

Samples of the ground pulp were cut wet on a Jones riffler, and the final cut was wet-screened on 200 mesh before being dried and screened completely to 200 mesh in a Ro-tap for 20 min. Sizing analyses were made of each feed, and the discharge samples were screened in duplicate.

Constant speed was maintained by voltage control, and was indicated continuously by a tachometer on the motor. Mill speeds were checked with a stop watch to insure a constant motor-mill ratio. All tests were run in the same manner.

## Data and Discussion

The data are shown in the accompanying figures and curves. Table 1 is a compilation of the results, and from it are drawn the following curves: units of surface per unit weight, Fig. 13; surface tons per hour, Fig. 14; net horsepower, Fig. 15; surface tons per horsepower-hour, Fig. 16. Table 2 is a typical data sheet taken at random from the notes. The results of each test were recorded, tabulated and calculated in this manner. The diagrams in the center represent the sieve analyses by plotting sieve sizes, as ordinates, against the percentages of material on

Table 1.—*Summary of Tests* 108 *to* 148, *Inclusive*

| Size of Mill, Inches | Mill Charge | | | Critical Speed, Per Cent. | Tons per Hour | Horse-power (Net) | Units New Surface per Unit Weight | Surface Tons per Hour | Surface Tons per Hp-hr. |
|---|---|---|---|---|---|---|---|---|---|
| | 1¼-in. Balls, Pounds | Ore, Pounds | Water, Pounds | | | | | | |
| 18 × 6 | 107 | 21.7 | 10.8 | 45 | 0.108 | 0.147 | 32.18 | 3.41 | 23.31 |
| | | | | 50 | | 0.174 | 38.85 | 4.20 | 24.20 |
| | | | | 55 | | 0.190 | 41.49 | 4.49 | 23.57 |
| | | | | 60 | | 0.211 | 43.92 | 4.74 | 22.45 |
| | | | | 65 | | 0.227 | 44.59 | 4.87 | 21.46 |
| | | | | 70 | | 0.206 | 44.10 | 4.76 | 23.11 |
| 24 × 6 | 190 | 38.5 | 19.2 | 45 | 0.192 | 0.294 | 40.32 | 7.74 | 26.32 |
| | | | | 50 | | 0.323 | 44.33 | 8.51 | 26.46 |
| | | | | 55 | | 0.362 | 48.74 | 9.36 | 25.83 |
| | | | | 60 | | 0.390 | 51.65 | 9.92 | 25.41 |
| | | | | 65 | | 0.420 | 52.43 | 10.07 | 23.95 |
| | | | | 70 | | 0.411 | 49.22 | 9.45 | 23.00 |
| | | | | 75 | | 0.406 | 47.21 | 9.06 | 22.33 |
| | | | | 80 | | 0.401 | 42.40 | 8.14 | 20.27 |
| | | | | 85 | | 0.358 | 38.95 | 7.48 | 20.87 |
| 30 × 6 | 297 | 60.2 | 30.1 | 45 | 0.301 | 0.582 | 43.62 | 13.14 | 22.55 |
| | | | | 50 | | 0.618 | 50.36 | 15.16 | 24.52 |
| | | | | 55 | | 0.683 | 52.97 | 15.94 | 23.36 |
| | | | | 60 | | 0.778 | 57.31 | 17.25 | 22.17 |
| | | | | 65 | | 0.846 | 60.36 | 18.17 | 21.49 |
| | | | | 70 | | 0.794 | 55.47 | 16.70 | 21.02 |
| | | | | 75 | | 0.736 | 53.22 | 16.02 | 21.77 |
| 36 × 6 | 427 | 86.6 | 43.3 | 45 | 0.433 | 0.940 | 50.47 | 21.86 | 23.27 |
| | | | | 50 | | 0.972 | 53.47 | 23.15 | 24.33 |
| | | | | 55 | | 1.064 | 59.53 | 25.78 | 24.23 |
| | | | | 60 | | 1.152 | 63.08 | 27.31 | 23.72 |
| | | | | 65 | | 1.250 | 63.55 | 27.51 | 21.98 |
| | | | | 70 | | 1.176 | 60.32 | 26.14 | 22.20 |
| | | | | 75 | | 1.103 | 55.60 | 24.07 | 21.85 |
| | | | | 80 | | 1.087 | 52.31 | 22.65 | 20.82 |
| 42 × 6 | 583 | 118.0 | 59.0 | 45 | 0.590 | 1.273 | 57.01 | 33.64 | 26.40 |
| | | | | 50 | | 1.416 | 64.63 | 38.17 | 26.95 |
| | | | | 55 | | 1.605 | 69.08 | 40.77 | 25.77 |
| | | | | 60 | | 1.750 | 74.08 | 43.70 | 24.96 |
| | | | | 65 | | 1.930 | 77.06 | 45.46 | 23.57 |
| | | | | 70 | | 1.730 | 70.70 | 41.69 | 24.10 |

the respective sieves, as bilateral abscissas. Thus, an ore containing much coarse material is represented by a diagram that is large near the top, while one containing much fine material is large near the bottom. The diagram does not assist in the calculations, but does give a compre-

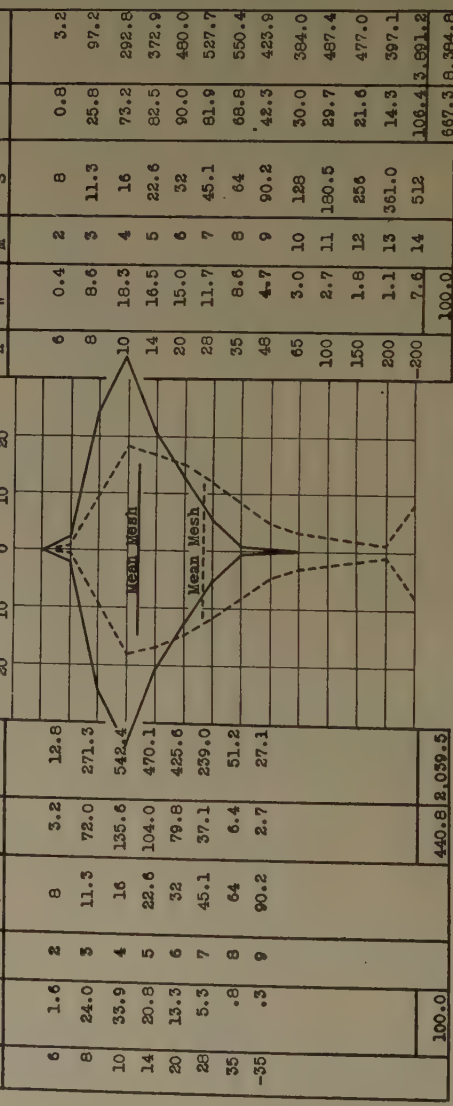
TABLE 2.—*Typical Data Sheet*

LABORATORY BALL MILL TEST NO. 135 – Tri-State Flint. June 14, 1929.

Size of Mill – 36" x 6". Speed – 65% of Critical. Ball Load –427 lbs. of 1-1|4" Balls.

Ore Load – 86.6 lbs. Moisture – 43.3 lbs. Solids – 67%. Duration of Run – 6 minutes.

| Actual Feed | | | | | | Actual Discharge | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mesh | Weight Per cent W | Lever Arm Mean Mesh M | Lever Arm Mean Surface S | Moments Mesh M x W | Moments Surface S x W | Mesh | Weight Per cent W | Lever Arm Mean Mesh M | Lever Arm Mean Surface S | Moments Mesh M x W | Moments Surface S x W |
| 6 | 1.6 | 2 | 8 | 3.2 | 12.8 | 6 | 0.4 | 2 | 8 | 0.8 | 3.2 |
| 8 | 24.0 | 3 | 11.3 | 72.0 | 271.3 | 8 | 8.6 | 3 | 11.3 | 25.8 | 97.2 |
| 10 | 33.9 | 4 | 16 | 135.6 | 542.4 | 10 | 18.3 | 4 | 16 | 73.2 | 292.8 |
| 14 | 20.8 | 5 | 22.6 | 104.0 | 470.1 | 14 | 16.5 | 5 | 22.6 | 82.5 | 372.9 |
| 20 | 13.3 | 6 | 32 | 79.8 | 425.6 | 20 | 15.0 | 6 | 32 | 90.0 | 480.0 |
| 28 | 5.3 | 7 | 45.1 | 37.1 | 239.0 | 28 | 11.7 | 7 | 45.1 | 81.9 | 527.7 |
| 35 | .8 | 8 | 64 | 6.4 | 51.2 | 35 | 8.6 | 8 | 64 | 68.8 | 550.4 |
| -35 | .3 | 9 | 90.2 | 2.7 | 27.1 | 48 | 4.7 | 9 | 90.2 | 42.3 | 423.9 |
| | | | | | | 65 | 3.0 | 10 | 128 | 30.0 | 384.0 |
| | | | | | | 100 | 2.7 | 11 | 180.5 | 29.7 | 487.4 |
| | | | | | | 150 | 1.8 | 12 | 256 | 21.6 | 477.0 |
| | | | | | | 200 | 1.1 | 13 | 361.0 | 14.3 | 397.1 |
| | | | | | | -200 | 7.6 | 14 | 512 | 106.4 | 3,891.2 |
| | 100.0 | | | 440.8 | 2,039.5 | | 100.0 | | | 667.3 | 8,934.8 |




Mean Mesh of Feed – 1.443 mm.

Mean Mesh of Discharge – 0.663 mm.

Reduction Ratio by Mean Mesh – 2.18

Mean Surface of Feed – 20.40

Mean Surface of Discharge – 83.85

Units of Surface Reduction (83.85 – 20.40) = 63.45

Tons Per Hour = 0.433

Horsepower Output = 1.250 (Net)

Tons Per H.P. Hour (0.433 ÷ 1.250) = 0.346

Surface Tons Per H.P. Hour (63.45 x 0.346) = 21.95

Surface Tons Per Hour (63.45 x 0.433) = 27.47

hensive idea of what has happened to the ore during grinding. All the tests made with any one mill constituted a series; five series were performed. The marked similarity of the grinding characteristics of the various series justifies the generalizations pertaining to the operation of these laboratory ball mills.

During all the tests the only predetermined variable was speed. Pulp density was maintained at 67 per cent. solids. The ball load, including voids, was 40 per cent. of the mill volume, and the total charge of balls, ore and water occupied 60 per cent. The weight of the ore was slightly over 20 per cent. of that of the balls.

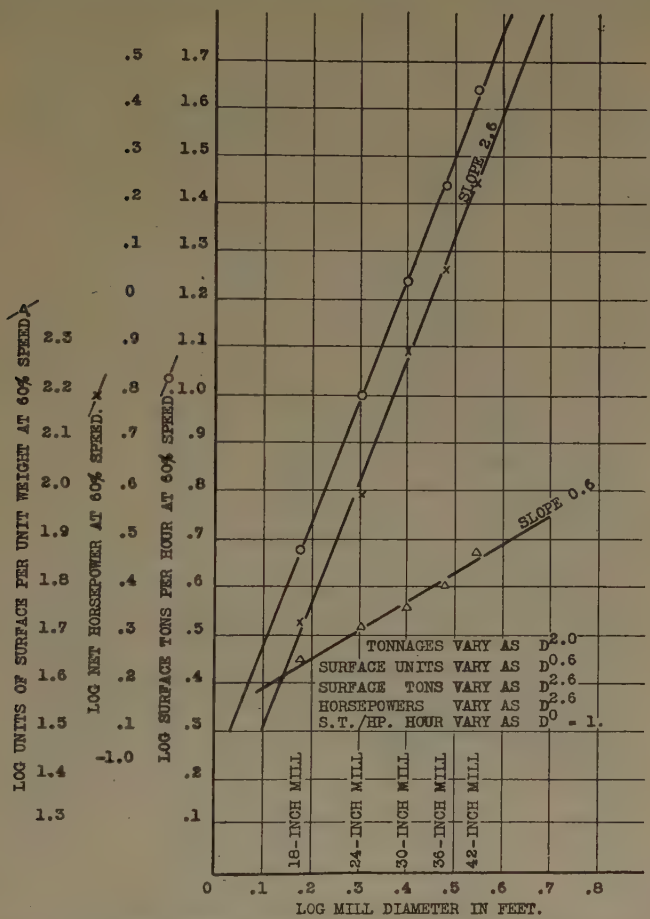



FIG. 20.—GRINDING CHARACTERISTICS AT 60 PER CENT. CRITICAL SPEED.

Table 1 and the data curves show that the units of surface per unit weight (Fig. 13), the surface tons per hour (Fig. 14), and the net horsepower (Fig. 15), showed the same tendency in every series. These values increased as speed increased to 65 per cent. of the critical. Beyond this speed they decreased. The surface tons per horsepower-hour (Fig. 16), however, reached its maximum at a lower speed; the most efficient grinding occurred at only 50 per cent. of the critical speed. This was true in each series. Below and above this speed the values of over-all

efficiency decreased except for a slight increase at a relatively very high speed. The lower speed (50 per cent.) resulted in 15 per cent. less crushing, but the power saving was 25 per cent., and thereby the efficiency was increased.

The tonnages treated in the five mills vary as the square of the diameters of the mills. The surface units per unit weight were found to

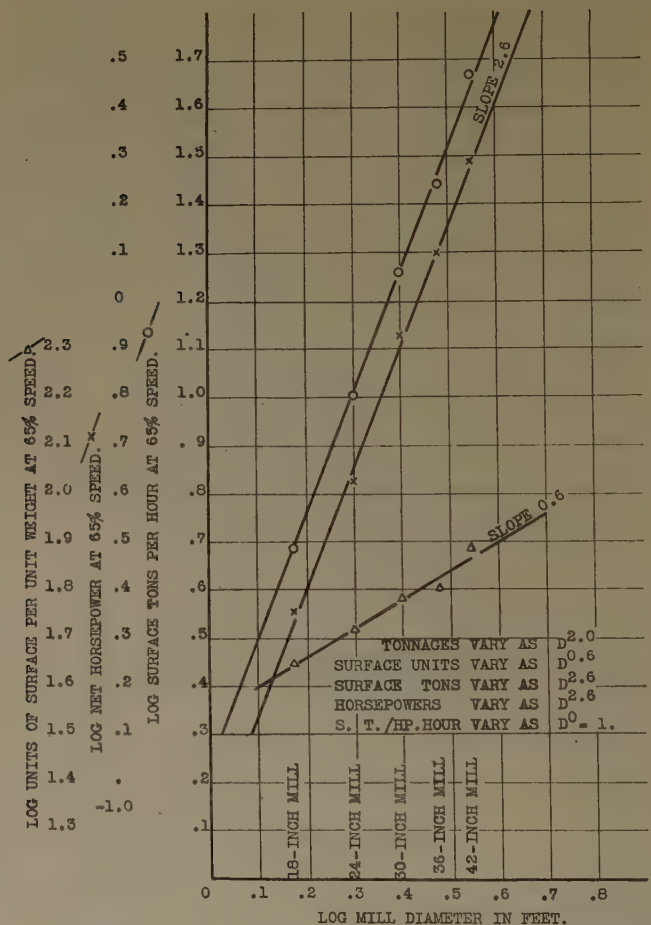



FIG. 21.—GRINDING CHARACTERISTICS AT 65 PER CENT. CRITICAL SPEED.

increase with the diameters of the mills. Under the same conditions more new surface was made per pound of ore in the large mills than in the small ones. This increase was proportional to the 0.6 power of the diameter. The surface tons, therefore, varied as the 2.6 power of the diameter. The horsepower also varied at the same rate. Consequently, the surface tons per horsepower-hour was about the same irrespective of the size of the mill. In Fig. 16 two curves show higher values than the

rest. A slight change in the hardness of the rock accounts for the seeming discrepancy; it was not absolutely uniform for the different series.

Logarithmic curves, in which the exponential functions of mill diameters appear as slopes, are shown in Figs. 17, 18, 19, 20, 21 and 22. The curves are from data for the respective speeds. Their regularity is significant. The several variables bear definite relationships to the diameter regardless of speed.

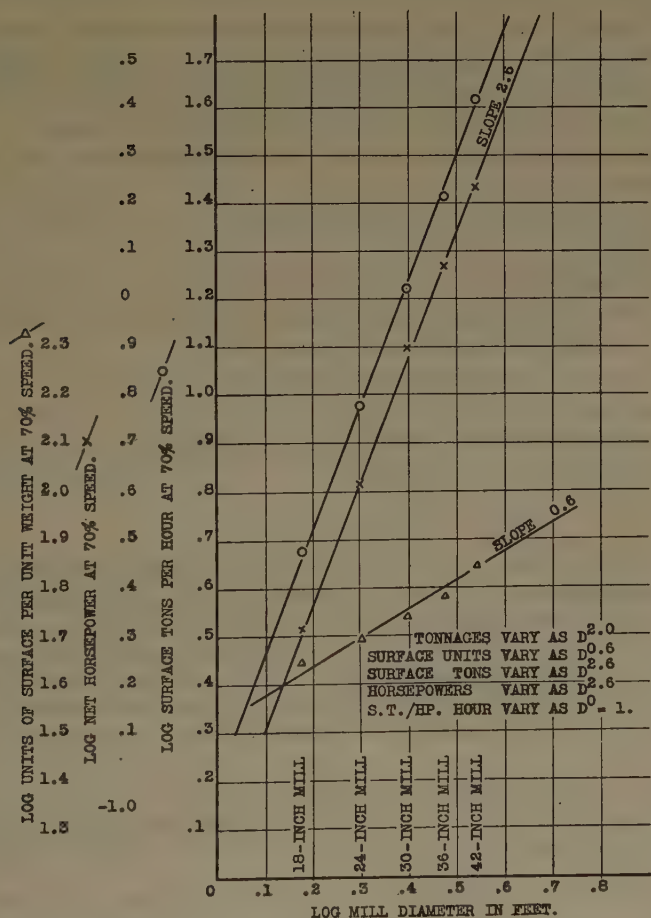



FIG. 22.—GRINDING CHARACTERISTICS AT 70 PER CENT. CRITICAL SPEED.

Inasmuch as the peripheral speeds of mills running at the same percentage of the critical varies as the square root, or 0.5 power, of the diameters, it follows that the surface units per unit weight (which varies at the 0.6 power of the diameter) vary approximately as the peripheral speed. Hence these results indicate that larger mills have the advantage of greater grinding capacity per unit of volume, but their over-all efficiency does not increase.

## Summary

1. Observations have been made with a 3-ft. squirrel-cage mill. A new theory of ball action has been advanced from this study, and a new formula of ball paths has been derived.

2. Laboratory tests with short ball mills in which slippage was reduced to a minimum have shown that the best grinding results were obtained at lower speeds than those hypothecated by previous theories. A speed of 65 per cent. of the critical gave the maximum grinding, while a speed of only 50 per cent. of the critical gave the most efficient grinding.

3. By comparing the grinding results of the mills of various diameters, it was found that at the same per cent. of the critical speed:

*a.* The units of surface per unit weight varied as the 0.6 power of the diameter;

*b.* The surface tons, or grinding capacity, varied as the 2.6 power of the diameter;

*c.* The horsepower also varied as the 2.6 power of the diameter;

*d.* The surface tons per horsepower-hour, or efficiency of grinding, was constant regardless of the diameter; and

*e.* The units of surface per unit weight varied approximately as the peripheral speed.

4. The larger mills showed larger grinding capacity per unit volume, but no increase in grinding efficiency.

## DISCUSSION

H. W. Hardinge, New York, N. Y.—I believe that the diameter or peripheral speed should be commensurate with the size of ball to be used. The smaller balls would require a lower peripheral speed, as their work is usually confined to grinding by contact rather than impact. It is on that theory and supposition that we have sometimes made changes in the ball mill operation, but I would rather not enter into discussion of anything of that sort, because I have not been in a ball mill while it was in operation, and figures sometimes will give a more demonstrable line of the operation than we can give from observation.

R. Gahl, Berkeley, Calif.—One of our local members recently applied some interesting new principles to ball mills. Perhaps somebody can tell us about Mr. Williamson's experiments?

J. C. Stroup, San Francisco, Calif.—We have had no figures. This installation is too new.

R. Gahl.—What are the dimensions of the large mills that are being used now in experimental manner at Inspiration?

J. C. Stroup.—They are 10½ by 10.

R. Gahl.—That is a good sized mill.

J. C. Stroup.—The floor space was the principal argument for the size of the mill. I do not know whether so large a size would have been used if 16,000 to 18,000 tons could have been handled in any other way. The original structure would handle about 4000 tons. The same structure now houses the 18,000-ton plant.

O. H. Johnson, Denver, Colo.—I am connected with the Marcy mills and we have built many large machines. We began with small units. The first Marcy ball mill manufactured was a 4-ft. machine. It was tested out at the Utah Copper in the early days of ball milling. The 6, 7 and 8-ft. diameters followed.

Several years ago at the Inspiration plant it was noticed that as the breast liners of the 8-ft. mill wore down, and the mills became larger in diameter therefore because the liners were thinner, *the capacity went up* with only a small increase in power. It was because of this observation and knowledge that the Inspiration Copper Co., about 1918, caused two sections of 8-ft. mills to be replaced by two sections of 9-ft. mills. Since that time those 9-ft. Marcy ball mills have been in operation and have proved entirely satisfactory. Figures covering a considerable period of time show less liner-steel consumption for the 9-ft. mill than for the 8-ft. size, and fewer kilowatt-hours per ton, indicating that the larger mill was the more efficient.

Since the operation of the 9-ft. mills at Inspiration others have been installed at the Andes. In providing power to drive the mills at Andes, 400-hp. motors were purchased. When the mills went into operation they took only about 350 hp., so recently we recommended the extension of these mills by adding 2 ft. to the shells, making them 9 by 9 ft. and using up the extra power available in the motors. This expansion was accomplished in the Andes by getting an increase in tonnage from these mills of about 25 per cent.

We feel that greater crushing efficiency is possible from larger grinding units, therefore we are laying out at present a 10-ft. Marcy ball mill, which means 10 ft. inside the shell liners when new.

W. L. Penick, Salt Lake City, Utah.—I represent the Hardinge Co. Fortunately, we have two installations of Hardinge ball mills in which there are 8-ft. dia. mills and 10-ft. dia. mills in the same plant. These two installations are rather far removed from one another. At the plant of the Consolidated Mining & Smelting Co., Kimberly, B. C., there are ten mills of 10 ft. dia. and seven mills of 8 ft. dia. The 8-ft. mills were installed first. Later, it was found that practically the same floor space could be utilized for 10-ft. mills. Definite tests have not yet been completed, but at present, I understand, the results indicate about 14 per cent. increased efficiency in tons per horsepower input for the 10-ft. mills when compared with the 8-ft. mills.

At one of the Mexican plants of the American Smelting & Refining Co. there are two 8-ft. by 36-in. and one 10-ft. by 48-in. Hardinge ball mills. Conservation of floor space was the factor that influenced the installation of the 10-ft. mill. Reports indicate an increased efficiency of a little better than 15 per cent. for the 10-ft. dia. as compared with the 8-ft. dia. mills.

A letter written by Frederick Laist, of the Anaconda Copper Mining Co., to H. W. Hardinge gives the results of several months of testing, comparing an 8-ft. dia. Hardinge mill with a 10-ft. dia. Hardinge mill. The test data indicated about 30 per cent. increased efficiency in tons per horsepower input in favor of the 10-ft. mill. However, certain favorable factors had to be taken into consideration, resulting in a calculated final increased efficiency of about 20 per cent.

These three examples show the relative efficiency of large-diameter and small-diameter ball mills.

Mr. Coghill says that in his test mill slippage was reduced to a minimum. I do not think Mr. Coghill's mill paralleled operating conditions. I believe there is slippage in ball mills between shell lining and ball charge, and I do not believe we can entirely eliminate slippage in actual practice with present methods of ore-grinding in ball mills. However, I do believe a great deal can be done by giving attention to the design of the lining. I know that some attention has been directed that way recently.

What size feed did Mr. Coghill use in his 3-ft. dia. laboratory test mill?

W. H. Coghill.—Through 3/16 and on 1-mm. round holes.

W. L. Penick.—How does that compare with actual milling-plant feed, when comparing the diameter of Mr. Coghill's mill being used for the grinding test with the diameter of a ball mill in a large milling plant?

W. H. Coghill.—Several sizes of balls were tried. The 1¼-in. balls did just as well as the larger ones.

W. L. Penick.—I do not believe that the work done by a ball mill is due to impact of the balls. I am thoroughly convinced that the major percentage of the grinding is the result of attrition. That is the way I explain the advantage of mills of larger diameter over mills of smaller diameter. The large-diameter mill has an increased height or depth of ball column, sometimes called crushing column, and within this ball or crushing column there is a slight movement of balls and ore, resulting in attrition within the ball charge. This attrition performs a large portion of ball mill grinding. Attrition from the balls rolling over each other, as a direct result of rotation of the ball mill, is also responsible for a large portion of ball mill grinding. Impact of the balls falling against the lining is responsible for only a small portion of the grinding.

O. H. Johnson.—The Marcy mills have reduced their speeds 10 per cent.

E. L. Oliver, San Francisco, Calif.—Mr. Coghill's remarks regarding the critical speeds are borne out in practice when the work of a ball mill with new liners and unworn lifters is compared to the work of the same mill when the liners have worn down. Any slipping of the ball mass on the shell means a certain amount of useless work and useless wear. When the lifters are high there is a relatively heavy load of balls in the bottom of the mill, between lifters, which are held stationary and do no grinding. The balls in this layer, several balls deep, are being lifted too far and become scattered, thus losing contact with other balls. These balls do no grinding but do greatly increase the unbalanced load, hence the horsepower. However, as the lifters wear down the balls between the lifters become active and increase the grinding. The evidence is borne out in many different types of mills that impact is only a minor part of the crushing and that attrition is the cause of the crushing. In the Williamson mill, with its plowshaped ends, the ball load has a double movement, both the usual rotary movement and a movement caused by the plows, which keeps the balls moving longitudinally back and forth in the mill, thereby giving increased grinding for the same weight of balls. As a matter of fact, in the Williamson mill the ball load is considerably less than in other mills of the same diameter but of the same tonnage capacity. The Williamson mill is always run at a considerably lower speed than a mill of the straight cylinder type because of the increased ball movement developed by the plowshaped ends. I have seen no data along these lines on the conical ball mills as compared with the cylindrical, but I should judge that the conical mill would approximate to a degree the motion of the balls in the Williamson mill; that is, there may be a longitudinal sliding of the balls which is not present in a cylindrical mill. Mr. Coghill has opened a field of investigation which certainly should be carried forward, and the economics of the problem from the dollars and cents standpoint should be studied, too, in relation to mill size. Minimum dollars expended per ton of output is the ideal condition. Capital cost has always to be considered, and at a rapid amortization rate too. This has a decided effect on true operating costs, which is frequently overlooked. If we follow out the theory laid down by Mr. Coghill, it would be immaterial whether we

put in five mills of one size or three of a larger size, provided the output was the same, but I believe that the larger the diameter of the mill, the less the capital cost per ton of output, not only on the ball mills themselves but on foundations and building space as well.

W. H. Coghill.—About 50 per cent. of the motive power in many of our old ball mills is spent in dead load, and dealing with that dead load is a good place to begin increasing ball mill efficiency.

What percentage of the total power expended is in dead load? Suppose you fill your mill with a normal weight, in the form of a solid mass, so that the mill will revolve like a flywheel. That will give the dead load figure. Then take another reading under normal operation and get the total power, and thus get the percentage of all energy that is put within the shell of the mill.

J. C. Stroup.—We have done considerable along that line. If my memory serves me right, it would not exceed 5 to 6 per cent. We have loaded the mill with liners and kept the mill approximately in balance. Once it has attained its speed, it uses very little power; my own guess would be that it certainly would not exceed 6 per cent.

I went into that in connection with a statement I heard some time ago, that 40 per cent. of power could be saved by a certain type of bearing. My idea was that if all the friction loss was saved it would not amount to 40 per cent.

O. H. Johnson.—I had built three large mills that carried a grinding medium of 50 tones each. I equipped them with S. K. F. bearings. The first mill was driven with a slip-ring type of motor. We found that we gained a low starting torque by using S. K. F. bearings. The two mills that went in subsequently were equipped with ordinary squirrel-cage motors. The running power is about the same as we figured it would be, so after the mill was accelerated, the S. K. F. bearings did not offer any particular advantage excepting in lubrication, care and expense.

W. L. Penick.—We have an experiment under way now, where we have two 8-ft. by 36-in. Hardinge ball mills operating. One is equipped with roller-type countershaft bearings and roller-type main bearings; the other is our standard construction. Thus far we have noted no material difference either in the starting or running load. Our conclusion is that a properly designed and properly lubricated sleeve bearing will function just as well as a roller bearing, when applied to ball mills. Doubtless this is due to the fact that ball mills operate at a relatively low speed, or revolutions per minute.

H. S. Martin, Garfield, Utah.—The Utah Copper Co. mounted one mill on the roller bearings and could not detect any power saving in the running load.

Member.—May I ask Mr. Coghill to repeat his definition of critical speed?

W. H. Coghill.—Critical speed is a speed at which, according to the laws of centrifugal force, balls on the outer circle do not leave the shell; that is, they centrifuge.

R. Gahl.—It is a very useful standard, although not so easy to observe in big mills.

W. H. Coghill.—Not in the operating mills, but it can be checked in the squirrel-cage mill and the observed path noted.

Member.—Which do you determine it on, the worn ball or the new ball?

W. H. Coghill.—The "critical speed" is mathematical. The formula is designed according to the laws of centrifugal force.

R. Gahl.—Mr. Butters raises the question of a rubber lining for ball mills.

J. H. Lewis, Berkeley, Calif.—The rubber lining for the ball mill was invented by Mr. Denny, in Ontario. The particular application for which the lining was put on at that time, as I gather, was for a tube mill or a straight cylindrical mill about 5 ft. dia., and under this condition of operation it was very successful, in fact, it is today. So on the success of that application, a great many people thought it would probably be successful on all applications. They went at it, but did not give due consideration to local conditions or mechanical conditions that prevailed. The result was that they went wild about rubber lining, the manufacturers as well as the consumers. Rubber lining is made of two different types, a wave type corresponding to the wave in cast iron, chrome or manganese steel liners today. Also the flat type held against the shell of the mill by clamp bars, using the type of clamp bar that would be used with a flat steel plate against the shell. After being in operation for a time, many of these liners failed, much to the chagrin of both parties concerned. It became necessary, then, to analyze the situation and find out why. After making one or two cursory examinations of rubber lining in mills, it was definitely concluded that the rubber lining is practical and economically applicable when within certain operating conditions. Those conditions must take in the speed of the mill, the size of the feed, the size of the ball and the dilution; in other words, all of the factors concerned that will bring about efficient grinding.

In gold mills, where the cast iron and steel balls are detrimental to the process, they still adhere to the use of pebbles. In that case, a pebble of 4 or 5 in. dia. does not weigh as much as a steel ball of 2 in. dia. Consequently the effect on the rubber lining is not as severe. We think the weight of the ball is the most detrimental factor in the use of rubber lining.

I did not hear Mr. Coghill's definition of critical speeds. There are a great many operators who do not appreciate the definition of critical speed. Employing speeds greater than the critical speed, the balls are carried to such a height that in dropping back they strike against the liners. This is the reason for considering mill speed in designing rubber liners. When the balls strike against the liners the force of the impact is terrific and causes a breakdown due to fatigue. The breakdown effect could be overcome by increasing the thickness of the liner to compensate the effect of the impact, but to do so will mean a greater capital outlay. Under these conditions it would be better to use manganese, chrome or cast iron liners.

It is not recommended on feeds of over 1 in. dia., because with feed coarser than that at the feed end of the mill, where there are no slimes to cover the balls and liners as much as at the discharge end, there will be a cutting effect on the rubber, which is not desirable.

C. E. Locke, Cambridge, Mass. (written discussion).—In September, 1929, I visited Rolla and had the privilege of actually seeing the mills in operation and observing the various phenomena of ball action described by the authors. Since the high cost of fine grinding still remains as the one factor that has not been reduced in the improved efficiency of flotation plants, the various investigations of the U. S. Bureau of Mines on crushing and grinding, at Rolla and elsewhere, are particularly pertinent, and the authors are to be congratulated on having contributed some new and valuable ideas to this important subject. In the squirrel-cage mill, I found that the crowding action and the segregation of the different sizes of balls, with the tendency of the larger balls to gather in the center of the mass, and the resulting ball paths were extremely well marked. The authors have also fully demonstrated the pushing effect on the leading ball by the balls behind it, which causes the leading ball to take a falling path or curve, which carries it farther than the parabolic path

assigned to it by earlier investigators. I have not undertaken to follow through the development of the mathematical formula, but this seems hardly necessary in view of the close agreement between the curve of actual fall and the curve computed by the formula.

The ball mill tests indicate that maximum grinding capacity is reached at a speed that is 65 per cent. of the critical speed while maximum grinding efficiency occurs at 50 per cent. of the critical speed. Grinding practice has been to run at about 75 per cent. of the critical speed, but it is significant that I found in a recent trip to the Southwest a definite tendency toward lower speeds as giving better results. The operators will probably never come down to the figure of 50 per cent., because capacity is their chief aim. If they could get both maximum capacity and maximum grinding efficiency at the same speed, there is no question what they would do, but it is certain that they will hesitate to cut down the capacity per mill and increase the size of installation in order to make the saving in power at 50 per cent. speed as compared to power required at the 65 per cent. speed point of maximum grinding.

While these 50 and 65 per cent. speed points have been established in the laboratory mills, they may have to be modified somewhat for mills of commercial size, where the slippage effect will vary with the length of the mill and the character of the lining. The testing mills at Rolla were very short and the effect of friction of the balls against the ends of the mill in tending to reduce slippage of the entire mass of balls is greater than in a mill having its length equal to or greater than its diameter. A rough liner would also reduce slippage effect and modify the speeds of maximum efficiency and maximum capacity. I would suggest that supplementary experiments be made in the laboratory with ball mills having lengths at least equal to the diameters, in order to throw more light on this point.

One conclusion reached from these laboratory tests is that grinding efficiency is constant regardless of the diameter of the mill. While the results clearly warrant this conclusion, it is in contradiction to the claim made that in mill operation ball mills of large diameter show a higher grinding efficiency in terms of tons per horsepower to the same fineness as compared to smaller mills in the same plants. This point needs to be cleared up.

E. W. Davis, Minneapolis, Minn. (written discussion).—In March, 1922, Dr. H. E. T. Haultain and F. C. Dyer presented a paper on Ball Paths in Tube Mills to the Canadian Institute of Mining and Metallurgy. This paper was largely a criticism of my paper on Fine Crushing in Ball Mills.[9] Dr. Haultain started to check the results of the experiments I had reported on ball paths and eventually developed a deep interest in the subject. After the publication of Dr. Haultain's paper, he continued his study of ball paths and by use of a slow-motion camera produced some remarkable photographs that were shown at the meeting of the Institute in August, 1923. The paper accompanying the moving pictures is published in volume 69 of the Transactions, but it was obviously impossible to publish any part of the moving pictures These pictures were remarkable and were taken at the rate of 120 exposures per second under the most exacting conditions. The pictures show a small ball mill, with glass ends, in operation and the dial of a tactometer, shown in the photographs, indicates the exact speed of the mill at all times.

Dr. Haultain was so kind as to bring a set of these films to the University of Minnesota for me to see before they were publicly exhibited. I was much interested in them, especially since they seem to disprove my experiments and theories. The moving pictures seemed to indicate that the speed of the mill should be increased above my findings in order to secure the ball paths I had indicated. In other words, my speeds seemed to be too low for the conditions I had shown to exist in the mill. The

[9] See footnote 4.

pictures had been carefully made and there was no question as to the accuracy of the data or the discrepancy between Dr. Haultain's results and mine. However, I contended that it was very difficult to see, even in these slow pictures, whether or not the balls were slipping on the lining of the mill and, if this slippage was considerable, this would account for the discrepancy. Dr. Haultain went back to Toronto and made a new set of motion pictures of a mill in operation, charged with balls and water. To this operating mill, he gradually added sand, and it is possible to see the effect of this additional sand on the paths taken by the balls. It was difficult to judge the magnitude of the effect of the sand addition by watching the pictures, so I had charts made showing the paths through which the balls actually passed.

After making these charts, I was pleased to find that the addition of the sand had reduced the slippage in the mill from about 9 per cent. to practically 0 per cent. and that the actual ball paths, when the slippage was at a minimum, were close to my theoretical curves. These charts and my discussion of Dr. Haultain's paper appear in volume 69 of the TRANSACTIONS. The pictures that Dr. Haultain prepared are worth considerable study by anyone interested in ball milling and certainly any new theory presented should satisfactorily pass the test of comparison with Dr. Haultain's pictures.

In comparing the ball-path curves shown in the paper by Gow, Campbell and Coghill with the curves shown in Dr. Haultain's moving-picture films, it was found that for the same ball-path curves, the author's speeds must be reduced considerably below those shown by Dr. Haultain. The paths determined by the "old formula" lie far inside the paths determined by the "new formula" as illustrated in Fig. 5 of this paper. Dr. Haultain's criticism of my curves were that they were slightly too wide, because there was always some slippage in the mill, and his moving-picture films seem to bear out this contention. According to the present authors, my curves are not nearly wide enough. Since the reduction of the slip in Dr. Haultain's mill brought his curves close to my theoretical curve, it seemed to me that in the mill operated by the authors of this paper, some condition must have existed that reduced to slip *below zero; i. e.*, made the balls cling to the lining of the mill longer than they ordinarily would. Fig. 2 shows a photograph of the mill used for observing the action of the balls. It is entirely possible that the 1-in. mesh wire screen that forms the ends of this mill, which are only 6 in. apart, would hold the 1¼-in. balls locked effectively and would carry the balls around the mill much farther than they would otherwise go. This seems to account for the great discrepancy between the theoretical paths as developed by the "old formula" and the "new formula."

I have not studied the details of this paper as I probably should but, as I have said, any new theory on ball paths must square itself with what is shown in Dr. Haultain's slow-moving picture films before I can give it serious consideration. I am surprised that the authors do not even mention Dr. Haultain's contribution, which I consider the one outstanding unimpeachable contribution to this subject, against which all theories must be tried.

H. A. WHITE, Dersley, Transvaal, South Africa (written discussion).—There can be no doubt that this paper has added considerably to our knowledge of the factors involved in ball milling and marks a distinct advance in the theory of the subject which naturally will be followed by improvements in actual practice.

The papers referred to by the authors might well have included that by Haultain and Dyer [*Trans.* A. I. M. E. (1923) **69**, 198]. In that paper, owing to the peculiar experimental method adopted, the authors found that the theoretical curves of flight required greater speed of revolution than indicated. Gow, Campbell and Coghill find the opposite effect, but their method, instead of exaggerating the effect of slip, provides a distinct tendency in the opposite direction. Nevertheless I do not

draw the facile deduction that the old theory of parabolic flight was more than a first approximation, and I consider that the second approximation offered by this paper is much nearer the actual facts. In a paper shortly to be read before the Chemical and Metallurgical and Mining Society of South Africa, I am offering a third approximation, which however I find anticipated to some extent by the remarks on "crowding" and in some of the curves in Fig. 4 which show paths outside the new theoretical curves suggested.

The term "critical speed" should certainly be adopted but it must be clearly defined as the speed at which the first layer of balls adheres to the rim. A much greater speed is required to cause all the balls to so adhere. The terms "cascade" and "cataract" may well be accepted as standard in the definition given, as they give an excellent mental picture of the two processes referred to. I would suggest that tube mills should include ball and pebble mills, the difference in the latter case merely referring to the grinding medium.

The photographs in Fig. 3, of the tubes loaded to 50 per cent, shows that at 10 per cent. of critical speed the kinetic angle of friction appears to be 38°, at 20 per cent., 44°, at 30 per cent., 48°, while the kinetic angle for steel balls at less than 1 r.p.m. will be found to be about 29°. These figures are suggestive and their effects upon theory will be dealt with in the paper already referred to. Incidentally, this paper has to be rewritten to some extent in order to take account of the authors' advance in theory.

No exception may be taken to the criteria employed, in deriving the new equation, though some statement as to angle $\beta$ might have made the matter clearer.

The deduction, from grinding tests, that 65 per cent. of critical speed gives maximum capacity is, of course, only true for 40 per cent. loading, and usually 50 to 55 per cent. loading is employed when a greater speed might be advantageous. The efficiency must be much the same at all speeds and loadings if relative size of balls and feed is not quite unsuitable to conditions maintained in accordance with the findings of Gross and Zimmerley, to which the authors refer. In any case the deductions made are based upon experimental conditions which do not closely imitate current practice, as too much ore and water are present and tubes are too short. It would be interesting if the authors would give us the foot-pounds per square inch corresponding with the surface-ton per horsepower unit adopted. Their results appear to indicate about 0.95 ft.-lb. per sq. in. new surface, against 0.03 as found by Gross and Zimmerley in their paper already mentioned. Even if the hopeless underestimate of the surface of −200-mesh product used by the authors be adjusted, it still shows a wide discrepancy, indicating that experimental conditions were very different and that there is still a large margin for improvement in tube mill work.

While cataracting at 75 to 85 per cent. of critical speed may suit pebble mills taking up to 1-in. particles, it may be more economical to use cascading at 50 to 70 per cent. for regrinding ball mills where particles in the feed are so small as to require little fall of the balls employed in order to break them without producing much fine dust beyond the range of technical requirements.

# Classifier Efficiency; an Experimental Study

By A. W. Fahrenwald,* Moscow, Idaho

(New York Meeting, February, 1930)

The function of the classifier in modern fine-grinding practice is to remove a finished product from the grinding-mill discharge, leaving material that needs further comminution. The classifier, therefore, makes two products: (1) "finished" product, which overflows the rim of the classifier tank, sometimes referred to as "slimes" or as "classifier overflow," and (2) "unfinished" product, which settles to the sloping bottom of the classifier tank and is removed by dragging or raking. This product is generally referred to as "sands" or "oversize."

One of the outstanding features of the closed-circuit classifier is its ability automatically to return the unfinished product of the ball-mill discharge to the feed end or scoop box of the ball mill. This is a distinct advantage because it avoids dilution of the ball-mill feed, and, furthermore, the particular method of removing the settled sand, by raking it up the inclined bottom of the classifier, gives a classifier discharge containing a minimum of water. This leads to maximum classifier efficiency, in this type of classifier, because the maximum volume of water is displaced upward by the settling sands.

The closed-circuit classifier is required to deliver a finished pulp of closely specified density requirements, therefore added hydraulic water generally is not permitted.

## Relation of Classifier Efficiency to Grinding Efficiency

The energy of crushing, and therefore the cost, according to Rittinger's Law,[1] is proportional to the new surface exposed in crushing. Since the new surface produced in crushing is nearly proportional to the reciprocals of the diameters crushed to, it is obvious that the cost of crushing in the finer sizes is tremendously greater than in the coarser sizes for equal ratios of reduction. High circulating load of finished sand in the circuit of the classifier and grinding mill is therefore obviously expensive practice. It is the classifier's function to reduce this to a minimum.

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[1] The correctness of this law has been definitely established by J. Gross and S. R. Zimmerley: *Repts. of Investigations*, U. S. Bur. Mines, Serial 2880 (1928). Also by G. Martin and coworkers: *Trans.* Ceram. Soc. (England) (1925–26) **25**, 51.

## Classifier Efficiency

It is the purpose of this paper to present a new experimental method of measuring classifier efficiency. A need for it may be brought out by a discussion of the present method and its limitations.

In the literature, the only method described of measuring performance of the closed-circuit classifier is based on sieve analyses of the classifier products. The formula used is:

$$E = \frac{10{,}000\,(b - a)(a - c)}{a(100 - a)(b - c)}$$

where $E$ = over-all efficiency of the classifier,
$a$ = percentage of finished sand in classifier feed,
$b$ = percentage of finished sand in classifier overflow,
$c$ = percentage of finished sand in classifier dragover.

This formula gives over-all classifier efficiency and is the original formula developed by H. W. Newton of the Dorr Co. The derivation is given, among other sources, in Taggart's Handbook of Ore Dressing, pp. 1235–1239. The efficiency of the classifier as a remover of finished product, granting that everything in the overflow is finished, is given by the formula

$$E_1 = \frac{100b(a - c)}{a(b - c)}$$

If tonnages are known these formulas are much simpler. The latter formula, of course, is identical with the well-known formula giving screening efficiency.

## Critical Consideration of Size Analysis as Basis of Measuring Classifier Efficiency

Some interesting mathematics may be indulged in to show the fallacy of sieve sizing as a basis of measuring classifier efficiency.

If all sand grains obtained by the use of a pair of sieves of small difference in mesh opening—for example adjacent sieves of the Tyler screen scale—behaved similarly in a rising column of water or fell at the same rate in a static body of water or other medium of appreciable density, classifier performance could be determined on a sizing analysis basis. This, however, is not the case because both grain density and configuration are variable and enter into the problem. If it is assumed that the classifying property of a sand grain is expressed by such a factor as $W/S$ (weight divided by surface) or specific weight of the grain, the fallacy of the sizing basis of measuring classifier efficiency may be shown in a few cases quantitatively.

Calculation of the $W/S$ of sand grains of various assumed configurations which pass an $r$-mm. square aperture follows:

A spherical grain that will pass an $r$-mm. square aperture (Fig. 1$A$) has a surface area, $S = 4\pi\left(\frac{r}{2}\right)^2$, and a weight, $W = \frac{4}{3}\pi\left(\frac{r}{2}\right)^3 d$. The $W/S$ of the grain is, therefore,

$$W/S = \frac{rd}{6}.$$

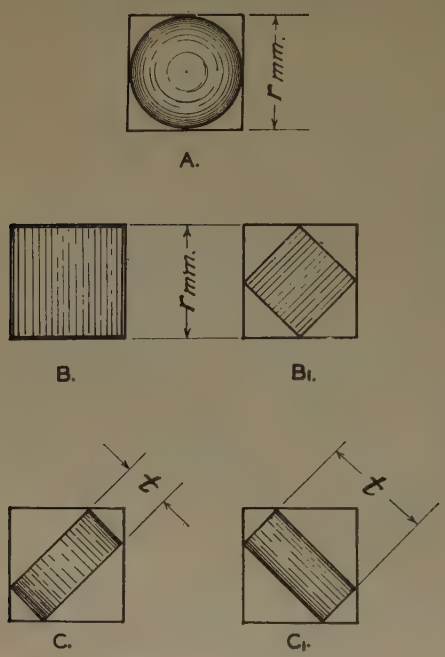


FIG. 1.—RELATION OF GRAIN CONFIGURATION TO THAT OF SIEVE OPENING.

The maximum cubical grain that will pass the $r$-mm. aperture (Fig. 1$B$) has a surface, $S = 6r^2$, and a weight, $W = r^3d$, and therefore

$$W/S = \frac{rd}{6}.$$

The cube of minimum $W/S$ (Fig. 1$B$) that will pass the $r$-mm. aperture, when one of its faces is parallel to the sieve surface, has a surface,

$$s = 6\left[\left(\frac{\sqrt{r^2}}{2}\right)^2\right] = 3r^2,$$

and a weight,

$$W = d\left(\frac{r^2}{2}\right)\sqrt{\frac{r^2}{2}} = \frac{r^3d\sqrt{\frac{1}{2}}}{2}$$

and

$$\frac{W}{S} = \frac{\frac{r^3d\sqrt{\frac{1}{2}}}{2}}{3r^2} = \frac{rd\sqrt{\frac{1}{2}}}{6}$$

If the cubical grain passes the aperture so that a diagonal through two apexes is normal to the sieve surface, the surface of the cube that just touches all four sides of the mesh is $S = 6\,\frac{3r^2}{4 + 2\sqrt{3}}$, the weight is $W = \frac{dr^3 \cdot 3^{3/2}}{(4+2\sqrt{3})^{3/2}}$ and $W/S = \frac{dr}{2\sqrt{12+6\sqrt{3}}}$.

The case of the cylindrical grain is more complicated. The disk or cylinder (Fig. 1$C$) of length $t$ that will just pass the $r$-mm. sieve opening has a surface

$$S = 2\pi\left(\frac{r\sqrt{2} - t}{2}\right)t + 2\pi\left(\frac{r\sqrt{2} - t}{2}\right)^2 = \frac{\pi(2r^2 - t^2)}{2}$$

and a weight,

$$W = \frac{\pi(r\sqrt{2} - t)^2 td}{4}$$

and, therefore, a

$$\frac{W}{S} = \frac{2\pi(\sqrt{2}\,r - t)^2 td}{4\pi(2\,r^2 - t^2)} = \frac{(\sqrt{2}\,r - t)td}{2(\sqrt{2}\,r + t)}$$

The cylindrical grain of maximum $W/S$, which just touches the four wires of the mesh, has a length, $t$ calculated as follows:

$$\begin{aligned}
\frac{\partial}{\partial t}\left(\frac{W}{S}\right) &= \frac{2(\sqrt{2}\,r + t)\cdot\dfrac{\partial(\sqrt{2}\,r - t)dt}{\partial t} - (\sqrt{2}\,r - t)dt\cdot\dfrac{\partial[2(\sqrt{2}\,r + t)]}{\partial t}}{4(\sqrt{2}\,r + t)^2} \\
&= \frac{2(\sqrt{2}\,r + t)(\sqrt{2}\,rd - 2dt) - (\sqrt{2}\,r - t)dt\cdot 2}{4(\sqrt{2}\,r + t)^2} \\
&= \frac{2(\sqrt{2}\,r + t)(\sqrt{2}\,r - 2t) - (\sqrt{2}\,r - t)t\cdot 2}{4(\sqrt{2}\,r + t)^2} \\
&= \frac{4r^2 - 2\sqrt{2}\,rt - 4t^2 - 2\sqrt{2}\,rt + 2t^2}{4(\sqrt{2}\,r + t)^2} \\
&= \frac{2t^2 - 4\sqrt{2}\,rt + 4r^2}{4(\sqrt{2}\,r + t)^2}
\end{aligned}$$

For minimum value of $\frac{W}{S}$, $\frac{\partial W}{\partial tS} = 0$ and therefore,

$$\frac{2t^2 + 4\sqrt{2}\,rt - 4r^2}{4(\sqrt{2}\,r + t)^2} = 0$$

or

$$t^2 + 2\sqrt{2}\,rt - 2r^2 = 0$$

and $t = -\sqrt{2}\,r \pm 2r$, but negative values have no meaning and when $W/S$ is a minimum,

$$t = -\sqrt{2}\,r + 2r = 0.584r$$

that is, the cylinder of maximum $W/S$, passing the aperture in the position specified, has a length just slightly more than one-half the aperture dimension. The $W/S$ for this cylinder is, then

$$\begin{aligned}
\frac{W}{S} &= \frac{(\sqrt{2}\,r - t)td}{2(\sqrt{2}\,r + t)} \\
&= \frac{(\sqrt{2}\,r - 0.58r)0.584\,rd}{2(\sqrt{2}\,r + 0.584r)} \\
&= \frac{0.48588r^2 d}{3.416r} \\
&= \frac{rd}{7.03}
\end{aligned}$$

There are tabulated below the $W/S$ values of grains of various assumed shapes which pass a square aperture under the conditions specified.

| Grain Configuration | $\frac{W}{S}$ Maximum | $\frac{W}{S}$ Minimum |
|---|---|---|
| Sphere | $\frac{rd}{6}$ | $\frac{rd}{6}$ |
| Cube | $\frac{rd}{6}$ | $\frac{\sqrt{\frac{1}{2}}rd}{6}$ |
| Cylinder | $\frac{rd}{7.03}$ | |

The $W/S$ of a grain is a function of the product of the aperture through which the grain just passed and its density times a constant, $k$, the value of which, except in the case of the cube and the sphere, is a function of the grain configuration. The general formula giving the $W/S$ of a grain, then, is:

$$\frac{W}{S} = krd$$

In Table 1 the constant $k$ of a 24/28 (av. dia. = 0.645 mm.) mesh, theoretically spherical grain, of an Ottawa silica sand grain, and of a crushed quartz grain, is given.

TABLE 1.—*Physical Constants of One* 24/28 *Mesh* (0.645 *Mm.*) *Grain*[a] $d_1 = 2.65$

| Grain | $V = 0.5283r^3$ Cu. Cm. | $W_1 = 0.5283r^3d$ Grams | $W = W_1 - V$ Grams | $\frac{W_1}{V}$ | $S = 3.1416r^3$ Sq. Cm. | Specific Wt. $= \frac{W}{S}$ Grams per Sq. Cm. | Constant $k$ |
|---|---|---|---|---|---|---|---|
| Sphere or cube (calc.) | 0.0001417 | 0.0003755 | 0.0002338 | 2.65 | 0.01307 | $17.72 \times 10^{-4}$ | 0.1666 |
| Ottawa sand (det.) | 0.0002030 | 0.000538 | 0.0003350 | 2.65 | 0.02570 | $13.04 \times 10^{-4}$ | 0.1216 |
| Crushed quartz (det.) | 0.0001885 | 0.000500 | 0.0003115 | 2.65 | 0.03200 | $9.73 \times 10^{-4}$ | 0.0916 |

[a] The volume and weight of the individual grain, in the case of the Ottawa sand and the crushed quartz sand, were determined by weighing a known number of grains and by measuring the volume of a relatively large weight of the grains by displacement in acetone. The surface is calculated from the data given by J. Gross and S. R. Zimmerley: Crushing and Grinding. I and II. See pages 7 and 27.

If it is desired to know the grain-size segregation that a classifier effects in the treatment of a given feed, a sieve-sizing analysis gives the information; however, if classifier efficiency is wanted, the sieve analysis basis is fundamentally wrong and misleading. Even when grain density is a constant factor, water sizing and square-mesh aperture sizing are not compatible.

This is further brought out in the graph of Fig. 2, which shows the arrangement of particles in an ideal classifier, with respect to their sizes and specific gravities. Shape is constant, but the feed is made up of grains differing widely, and uniformly, in size and specific gravity.

Assuming a classifier separation at $x$ mm. size, the nature and relative quantities of classifier products may be shown by passing lines through the classifier column in the proper directions.

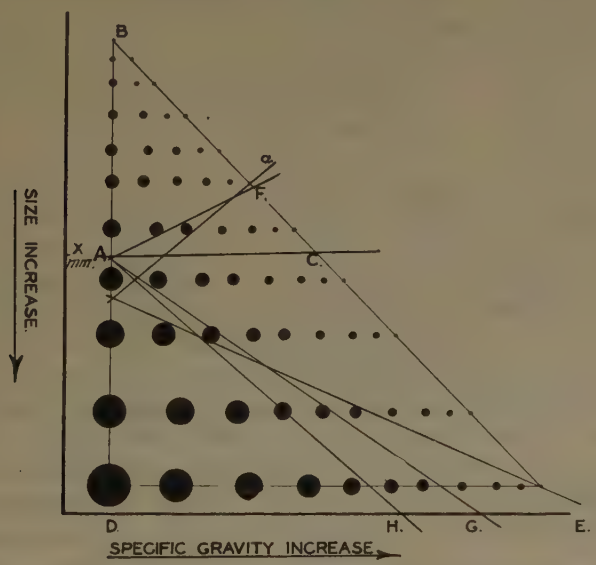


FIG. 2.—CROSS-SECTION OF IDEAL CLASSIFICATION WHEN SIZE AND SPECIFIC GRAVITY OF GRAINS ARE VARIABLE BUT SHAPE IS CONSTANT.

The horizontal line $AC$ divides the classifier input into two perfect products; namely, finished above the line $AC$ and unfinished below this line. For a classifier less than 100 per cent. perfect some finished product, represented by the portion $CAF$, remains with the unfinished, and the extent or degree of classification is represented by the portions of the graph above (finished) and below (unfinished) the sloping line $AF$. Referring to the formula $E_1 = \frac{100b(a-c)}{a(b-c)}$, and tying it into this graph, we have:

$$CAB = a$$
$$CADE = 100 - a$$
$$CAF = c$$
$$100 = b$$

Therefore $$E = 100\frac{(100)(a-c)}{a(100-c)} = \frac{10{,}000(a-c)}{a(100-c)}$$

and since $AC$ is horizontal, and therefore represents perfect classification,

$$c = 0,$$

$$\text{and } E = \frac{10{,}000(a - 0)}{a(100 - 0)} = \frac{10{,}000a}{100a} = 100 \text{ per cent. efficiency.}$$

If classification were effected entirely on the basis of size, perfect separation at $x$ mm. is indicated by the portion of the feed above and to the right of line $AH$. Less than perfect separation at the $x$ mm. size is represented by a line such as $AG$, and

$$EBAH = a_1$$
$$HAD = 100 - a$$
$$GAH = c_1$$
$$100 = b_1$$

$$\text{and } E_1 = \frac{10{,}000(a_1 - c_1)}{a_1(100 - c_1)}, \text{ and when } GAH = 0 = c_1$$

$E_1 = 100$ per cent. efficiency on the basis of sieve analyses.

The two efficiency formulas are identical, and for determining screening efficiency it is proper to determine the values of $a_1$ and $c_1$ on the basis of sieve analyses. However, it is obvious from Fig. 2 that it is scientifically permissible to determine the values of $a$ and $c$ by sizing only when the material in question is uniform in density and shape. In that case the sloping line $AG$ should approach the horizontal position occupied by $AC$. However, when density of grain is variable, theoretically $a$ and $c$ should be determined on the principle of operation of the classifier.

## Experimental Method Developed

Previous research[5] by the writer suggested to him a method based on the fundamental factors involved in classification. In Fig. 3 is shown the experimental set-up used. It consists of a glass tube $t$, of suitable bore and length, provided at its top with a funnel $f$ and at its tapered bottom with provision for admitting into the tube adjustable rising currents of water to meet the requirement of the experiment. The provision is a flask pressure chamber $p$, into which water is controllably admitted through a valve $v$ under constant pressure. The amount of water admitted is dictated by the size and specific gravity of the largest grains in the charge to be studied. The funnel is large enough so that material may be fed to the tube without overflowing any of it through the funnel outlet.

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[5] A. W. Fahrenwald: Hydraulic Classification, Its Theory, Mechanical Development, and Application in Ore Dressing. U. S. Bur. Mines *Tech. Paper* 403 (1926).

Stratification, Theory, and Application in Ore Dressing. *Min. & Met.* (1926) **7**, 437.

The size of the charge to be analyzed is largely determined by the nature of the ore. From 100 to 1000 g. are used, depending on the case in hand. Tubes the size of ordinary burettes to 1 in. dia. or more and 2 ft. or more long may be used. A small charge should not be used in a large tube, nor a large charge in a small tube.

The charge—it need not be weighed out accurately—is washed carefully into the funnel and water is added to give a just hindered-settling condition in the sands at the bottom of the tube. This condition should be allowed to obtain for several minutes, or until the sand grains have had time to adjust themselves and to find their proper static environment with respect to other grains.

The fluid teeter column is now stirred in a slow circular motion by hand, with a long glass rod, and the water is entirely cut off. The stirring is continued until the charge is entirely compacted, the stirring rod being raised slowly to keep the lower end just above the gradually forming compacted bed. This procedure is to prevent eddy currents in the teeter column, and serves the desired purpose. The stirring is the equivalent of rotating the tube, as in some earlier experiments, but is a more convenient method.

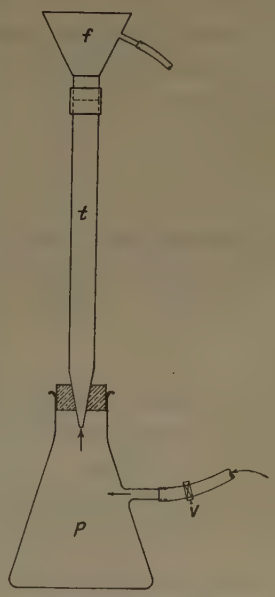

FIG. 3.—HYDRAULIC SIZER SET-UP.

The compacted column of sands in the tube, in which classification of the grains is probably as nearly perfect as may be approached experimentally, now is in condition to be removed from the tube. The removal is accomplished by a siphon method. It should be mentioned here, too, that the compacted bed is removed with much more facility than when the same material is in teeter.

The siphon consists of a pair of glass tubes connected with a rubber tube. The siphon is made operative by placing one tube in the water in the funnel and sucking at the other end with the mouth. Water should be admitted to the funnel from a suitable source in continuous flow before proceeding with the withdrawal of the sands. This is to replace in the column as much water as is removed through the siphon. The end of the tube in the funnel is now lowered toward the compacted bed of sands and as much of the column siphoned out into a pan as desired.

The compacted column may be cut into as many individual small layers as desired. The greater the number of cuts, mathematically, the more nearly the experiment approaches the ideal. It is well to graduate the tube so that approximately equal quantities may be drawn off, if

that seems desirable. This is an extremely useful technique in the laboratory study of many ores.

The individual small increments, which, when added up, comprise the whole, are next dried and sieve-sized. If only classifier efficiency is desired, only determination of maximum grain of each product is necessary. If a complete picture of a vertical cross-section through the ideal classification is desired, complete sieve and chemical analyses of each cut is made. Also, if a complete knowledge of the concentratibility of the ore is desired, heavy liquid or microscopic analysis of each weight increment is useful. This same technique gives valuable data in studying flotation tailing.

## Experimental Data

In Tables 2, 3 and 4 are given the results of experimental analyses of classifier products from the Morning Mill at Mullan, Idaho, of the Federal Mining and Smelting Co. The number of the increments.

Table 2.—*Ideal Classification Analysis of Feed, Morning Mill*

| SAMPLE NO. | WT. GRAMS | WT. % | WT. % CUM. | +35 | +42 | +48 | +60 | +65 | +80 | +100 | +115 | +150 | +170 | +200 | -200 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | FEDERAL TYPE CLASSIFIER – FEED. | | | | | | | | | | | |
| 1 | 21.20 | 11.16 | 11.16 | | | | | | | | | | | | 21.20 |
| 2 | 4.63 | 2.42 | 13.58 | | | | | | | | | | | | 4.63 |
| 3 | 6.25 | 3.27 | 16.85 | | | | | | | | | | | 0.95 | 5.30 |
| 4 | 6.30 | 3.29 | 20.14 | | | | | | | | | 0.86 | 0.88 | 0.71 | 3.85 |
| 5 | 7.91 | 4.14 | 24.28 | | | | | | | | 1.18 | 1.47 | 1.57 | 1.08 | 2.61 |
| 6 | 9.16 | 4.78 | 29.06 | | | | | | | 2.37 | 1.37 | 1.71 | 1.51 | 0.62 | 1.58 |
| 7 | 7.95 | 4.16 | 33.22 | | | | | | 1.77 | 2.25 | 0.92 | 1.30 | 0.78 | 0.30 | 0.63 |
| 8 | 8.67 | 4.53 | 37.75 | | | | | 2.20 | 0.56 | 2.32 | 0.87 | 1.27 | 0.72 | 0.20 | 0.53 |
| 9 | 10.37 | 5.42 | 43.17 | | | | 1.06 | 2.15 | 0.60 | 2.72 | 1.07 | 1.35 | 0.55 | 0.17 | 0.70 |
| 10 | 11.85 | 6.18 | 49.35 | | | | 1.92 | 2.91 | 0.73 | 2.80 | 1.17 | 1.25 | 0.50 | 0.09 | 0.48 |
| 11 | 12.63 | 6.60 | 55.95 | | | 1.40 | 1.80 | 3.15 | 0.85 | 2.62 | 0.98 | 0.90 | 0.42 | 0.11 | 0.42 |
| 12 | 13.90 | 7.26 | 63.21 | | 1.30 | 1.25 | 2.20 | 3.23 | 0.51 | 2.65 | 0.93 | 0.83 | 0.43 | 0.10 | 0.47 |
| 13 | 70.31 | 36.79 | 36.79 | | 25.15 | 7.10 | 9.37 | 12.00 | 1.57 | 7.52 | 2.37 | 2.30 | 1.10 | 0.35 | 1.48 |
| TOTAL WT. | 191.13 | 100.00 | 100.00 | | 26.45 | 9.75 | 16.35 | 25.64 | 6.59 | 25.25 | 10.86 | 13.24 | 8.54 | 4.68 | 43.88 |
| WT. % | 100.00 | | | | 13.54 | 5.10 | 8.55 | 13.40 | 3.44 | 13.20 | 5.68 | 6.93 | 4.46 | 2.44 | 23.26 |
| WT. % CUM. | 100.00 | | | → | 13.54 | 18.64 | 27.19 | 40.59 | 44.03 | 57.23 | 62.91 | 69.84 | 74.30 | 76.74 | 23.26 |
| WT. % CUM. | 100.00 | | | ← | 13.54 | 86.66 | 81.56 | 73.01 | 59.61 | 56.17 | 42.97 | 37.29 | 30.36 | 25.90 | 23.26 |

(No. 1 being the top increment), weight, weight per cent., weight per cent. cumulative, and sieve analysis of each increment are given. The summation of the sieve analyses of all of the increments gives the sieve analysis of the head sample. We may thus compare the products as analyzed by sieve sizing with the same products analyzed by hydraulic sizing.

This comparison is made in Table 5. The percentage of the total feed that should overflow the ideal classifier at any given sieve mesh opening is given in column 3. The percentage of the total feed that will pass a

given sieve opening, as indicated by a sieve analysis, is given in column 4. The difference is given in the final column.

TABLE 3.—*Ideal Classification Analysis of Dragover Sands, Morning Mill*

| SAMPLE NO. | WT. GRAMS | WT. % | WT. % CUM. | +35 | +42 | +48 | +60 | +65 | +80 | +100 | +115 | +150 | +170 | +200 | -200 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | FEDERAL TYPE CLASSIFIER—DRAGOVER | | | | | | | | | | | |
| 1 | 4.72 | 4.73 | 4.73 | | | | | | | | | | | | 4.72 |
| 2 | 2.83 | 2.83 | 7.56 | | | | | | | | | 0.30 | 0.15 | 0.20 | 2.18 |
| 3 | 5.90 | 5.91 | 13.47 | | | | | | 0.12 | 0.55 | 0.48 | 1.01 | 0.95 | 0.47 | 2.22 |
| 4 | 6.13 | 6.14 | 19.61 | | | | | 0.30 | 0.23 | 1.30 | 0.82 | 0.96 | 0.87 | 0.38 | 1.27 |
| 5 | 7.09 | 7.10 | 26.71 | | | | | 1.00 | 0.58 | 1.66 | 0.92 | 1.02 | 0.80 | 0.28 | 0.83 |
| 6 | 6.61 | 6.62 | 33.33 | | | | | 1.87 | 0.49 | 1.58 | 0.82 | 0.84 | 0.48 | 0.13 | 0.47 |
| 7 | 6.68 | 6.69 | 40.02 | | | | | 2.31 | 0.48 | 1.38 | 0.73 | 0.80 | 0.36 | 0.10 | 0.45 |
| 8 | 7.80 | 7.81 | 47.83 | | | | | 3.54 | 0.47 | 1.37 | 0.80 | 0.78 | 0.29 | 0.08 | 0.47 |
| 9 | 5.97 | 5.98 | 53.81 | | | | | 3.00 | 0.20 | 1.20 | 0.48 | 0.46 | 0.21 | 0.05 | 0.37 |
| 10 | 5.28 | 5.29 | 59.10 | | | | | 3.12 | 0.15 | 0.84 | 0.34 | 0.34 | 0.14 | 0.05 | 0.30 |
| 11 | 6.52 | 6.53 | 65.63 | | | | | 4.15 | 0.12 | 1.05 | 0.33 | 0.30 | 0.17 | 0.05 | 0.35 |
| 12 | 34.32 | 34.37 | 34.37 | | | | | 27.50 | 0.55 | 2.50 | 0.72 | 1.10 | 0.68 | 0.35 | 0.92 |
| TOTAL WT. | 99.85 | 100.00 | 100.00 | | | | | 46.79 | 3.39 | 13.43 | 6.44 | 7.91 | 5.10 | 2.15 | 14.55 |
| WT. % | 100.00 | | | | | | | 46.80 | 3.39 | 13.48 | 6.45 | 7.93 | 5.11 | 2.15 | 14.69 |
| WT. % CUM. | 100.00 | | | → | | | | 46.80 | 50.19 | 63.67 | 70.12 | 78.05 | 83.16 | 85.31 | 14.69 |
| WT. % CUM. | 100.00 | | | ← | | | | 46.80 | 53.20 | 49.81 | 36.33 | 29.88 | 21.95 | 16.84 | 14.69 |

Considering the classifier feed and assuming a separation at 100 mesh, the percentage of material in the feed, as indicated by the hydraulic test, which should overflow the classifier and leave the crushing system as finished sand, is 24.5 per cent. Sieve analysis of the feed shows that there is present 42.97 per cent. of −100-mesh material, the difference being the large figure of 18.47 per cent.

TABLE 4.—*Ideal Classification Analysis of Overflow, Morning Mill*

| SAMPLE NO. | WT. GRAMS | WT. % | WT. % CUM. | +35 | +42 | +48 | +60 | +65 | +80 | +100 | +115 | +150 | +170 | +200 | -200 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | FEDERAL TYPE CLASSIFIER—OVER FLOW. | | | | | | | | | | | |
| 1 | 57.90 | 56.40 | 56.40 | | | | | | | | | | | | 57.90 |
| 2 | 2.70 | 2.63 | 59.03 | | | | | | | | | | | | 2.70 |
| 3 | 3.55 | 3.46 | 62.49 | | | | | | | | | | | 0.20 | 3.35 |
| 4 | 4.84 | 4.62 | 67.11 | | | | | | | | | | 0.17 | 0.45 | 4.22 |
| 5 | 2.16 | 2.10 | 69.21 | | | | | | | | | | 0.19 | 0.27 | 1.70 |
| 6 | 4.17 | 4.01 | 73.22 | | | | | | | | | 0.41 | 1.06 | 0.60 | 2.10 |
| 7 | 6.38 | 6.16 | 79.38 | | | | | | | 0.57 | 0.83 | 1.37 | 1.29 | 0.52 | 1.80 |
| 8 | 4.83 | 4.71 | 84.09 | | | | | | | 0.86 | 0.66 | 0.82 | 0.82 | 0.35 | 1.32 |
| 9 | 5.05 | 4.91 | 88.99 | | | | | 0.22 | 0.27 | 1.30 | 0.76 | 0.75 | 0.70 | 0.20 | 0.85 |
| 10 | 11.16 | 11.01 | 11.01 | | | | | 3.58 | 0.53 | 2.42 | 1.20 | 1.35 | 0.79 | 0.32 | 0.97 |
| TOTAL WT. | 102.74 | 100.00 | 100.00 | | | | | 3.80 | 0.80 | 5.15 | 3.45 | 4.70 | 5.02 | 2.91 | 76.91 |
| WT. % | 100.00 | | | | | | | 3.70 | 0.76 | 5.02 | 3.34 | 4.58 | 4.88 | 2.83 | 74.89 |
| WT. % CUM. | 100.00 | | | | | | | 3.70 | 4.46 | 9.48 | 12.82 | 17.40 | 22.28 | 25.11 | 74.89 |
| WT. % CUM | 100.00 | | | | | | | 3.70 | 96.30 | 95.54 | 90.52 | 87.18 | 82.60 | 77.72 | 74.89 |

Similar comparisons may be made at any other assumed overflow mesh, and always there is the striking difference between what actually

will overflow, as indicated by the hydraulic test, and the percentage of material in the feed, as indicated by sieve analysis. These figures begin to indicate the fundamental unfitness of the sieve analysis as a basis of gaging classifier performance.

Now turn to a consideration of the classifier (dragover) sands, Table 3. Still assume that the classifier was making a separation at 100 mesh. By the hydraulic test there is actually 10.75 per cent. of finished product in the unfinished sand, which returns to the ball mill for further comminution. The sieve analysis shows 36.33 per cent. of finished sands in the unfinished product, a difference of 25.58 per cent.

Referring to the classifier overflow, Table 4. At a 100-mesh separation, the overflow actually contains 79.0 per cent. finished and 21.0 per cent. unfinished, while a sieve analysis of the overflow shows 90.52 per cent. finished and 9.48 per cent. unfinished product.

TABLE 5.—*Comparison of Classifier Performance by Hydraulic Analysis and by Sieve Analysis*

Ore from Morning Mill, Mullan, Idaho

| Material | Separation, Mesh | Finished Product, Per Cent. | | |
|---|---|---|---|---|
| | | Theoretical[a] | By Sizing | Difference |
| Feed from Table 2 | 200 | 13.58 | 23.26 | 9.78 |
| | 170 | 16.00 | 25.90 | 9.90 |
| | 150 | 18.00 | 30.36 | 12.36 |
| | 115 | 20.50 | 37.29 | 16.79 |
| | 100 | 24.50 | 42.97 | 18.47 |
| | 80 | 29.00 | 56.17 | 27.17 |
| | 65 | 33.50 | 59.61 | 26.11 |
| Dragover sands from Table 3 | 200 | 4.72 | 14.69 | 9.97 |
| | 170 | 5.75 | 16.84 | 11.09 |
| | 150 | 6.75 | 21.95 | 15.20 |
| | 115 | 7.70 | 29.88 | 22.18 |
| | 100 | 10.75 | 36.33 | 25.58 |
| | 80 | 13.50 | 49.81 | 36.31 |
| | 65 | 19.50 | 53.20 | 33.70 |
| Overflow slimes from Table 4 | 200 | 59.03 | 74.89 | 15.86 |
| | 170 | 62.49 | 77.72 | 15.23 |
| | 150 | 69.21 | 82.60 | 13.39 |
| | 115 | 73.22 | 87.18 | 14.96 |
| | 100 | 79.00 | 90.52 | 11.52 |
| | 80 | 84.09 | 95.54 | 11.45 |
| | 65 | 88.00 | 96.30 | 8.30 |

[a] Calculated from graph plotting per cent. through vs. cumulative weight per cent.

The difference in percentage of finished in unfinished product, as indicated by the hydraulic test and as indicated by sieve analysis, is

less for the finer overflows than for the coarser overflows in the case of the feed and the dragover products; and the reverse of this order is the case for the classifier overflow. This is quite in order with effect of decrease in size and influence of viscous surface films on hindered-settling ratios.

Using the over-all efficiency formula, page 83, let us examine the efficiencies of the classification recorded herein. Assume, as we have done above, a classifier separation at 100-mesh, then from the data of Table 5

$$a = 24.50$$
$$b = 79.00$$
$$c = 10.75$$

Then, $E = \dfrac{10{,}000(79.00 - 24.5)(24.50 - 10.75)}{24.50(100 - 24.50)(79.00 - 10.75)} = 59.28$ per cent. efficiency on the basis of analyses of classifier products by the hydraulic test.

The efficiency of classification at 100-mesh separation, on the basis of sieve analyses is:

$$a_1 = 42.97$$
$$b_1 = 90.52$$
$$c_1 = 36.33$$

and $E = \dfrac{10{,}000(90.52 - 42.97)(42.97 - 36.33)}{42.97(100 - 42.97)(90.52 - 36.33)} = 22.11$ per cent. efficiency.

At 170-mesh separation the classifier efficiency, by the hydraulic test, is:

$$E = \frac{10{,}000(62.49 - 16.00)(16.00 - 5.75)}{16(100 - 16)(62.49 - 5.75)} = 62.50 \text{ per cent.}$$

and by sieve analysis, 40.20 per cent.

## Summary and Conclusions

1. The ratio "weight divided by surface" of sand grains is a widely varying factor for ore grains passing a given sieve aperture.

2. Closed-circuit classifier efficiency is not theoretically accurately expressed on the basis of sieve analysis.

3. Closed-circuit classifier efficiency shows to much better advantage on the basis of ideal classification than on the basis of sieve analyses.

4. The efficiency of the classification studied is about 60 per cent. This suggests opportunity for useful further research in the field of this type of classification.

5. Classifier efficiency on the basis of removal of finished product shows up to better advantage than on the basis of over-all efficiency.

# Differential Grinding Applied to Tailing Retreatment

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(San Francisco Meeting, October, 1929)

The Missouri-Kansas Zinc Corpn., operating in the Waco district, 15 miles northwest of Joplin, Mo., owns large tailing piles made during milling operations of the years 1918–28 by the Butte-Kansas, Acme, and Barnsdall mining companies, whose holdings have been purchased and consolidated under the ownership of the Missouri-Kansas Zinc Corpn. These tailings had been considered too low in value to be worth retreating by the ordinary methods.

C. Erb Wuensch, consulting engineer of the Missouri-Kansas Zinc Corpn., noted the difference in the type of tailing from upper-level and lower-level ore. The latter contained hard lime chats. He also found that mill losses had been due to particles of blende on the corners or sides of the chats and to the existence of soft, porous, cellular, lime chats containing varying amounts of blende. He conceived the idea that a quick grind in rolls or ball mills might change the type of the material so that jigging could make a clean tailing for discard and a partly concentrated product sufficient in blende content to justify the expense of fine grinding in ball mills to free the mineral entirely. A laboratory was equipped with the necessary machines and the writers were assigned the problem of developing a method of retreating the tailings.

## Laboratory Testing

From preliminary drill sampling of each pile was obtained the blende content, the soluble sulfate content, and the general characteristics of the material to be treated. The tailings were a mixture of lime and flint with some shale.

Visual examination showed most of the blende to be in the dolomite and very little in the flint, although there were some flint particles with blende on the cleavages. The blende was found as particles on the corners or cleavage faces in one type of chat and in another disseminated in a soft, porous, cellular lime. Because of the porosity of the latter type of chat, the apparent specific gravity, under hindered-settling conditions, is less than that of a solid piece of lime or flint. That it

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cannot be settled by jigging or other gravity methods of concentration was conclusively proved by tests.

No ball mills had been used, up to this time, in the Waco district. A cost of 25 to 50 c. per ton, established by the practice in the Picher field, was prohibitive if applied to all the tailings, hence some preliminary concentration before thorough grinding was considered essential to an economic process.

Considerable time was spent in jigging tests of all kinds, using a small hand jig and a small Bendelari jig. Sized and unsized feeds were treated. Sieves of different sizes and shapes were tried, changes were made from time to time in depth of bed, number and length of strokes, amounts of pulsion and suction, and various materials were used for bedding. These experiments were all confined to +20-mesh material and no free mineral was encountered. Free mineral was known to exist in the −20-mesh material but as these finer sizes were much richer than the coarse, no difficulty was anticipated in retreating them by tabling and flotation.

Exhaustive tests by jigging and by classifying +20-mesh material showed that a satisfactory preliminary concentration could not be made by wet gravity methods. Concentration of the porous type of chat was poor and that of the other type only partial.

Because the average grade of the tailings to be treated was very low, it was necessary to attain a very low assay on the secondary tailings to make any process of economic value.

## Ball Mill Grinding versus Roll Crushing

Preliminary concentration by differential grinding in ball mills and rolls was also investigated. The material used was Barnsdall No. 3 dump tailing, +20-mesh size, assaying actual blende, 1.24 per cent.; soluble zinc, 0.15 per cent. Screen analysis of the feed is shown in Table 1.

Table 1.—*Screen Analysis of Feed*

| | Blende Assay, Per Cent. | Weight, Per Cent. | Cum. Wt., Per Cent. | Value, Per Cent. | Cum. Value, Per Cent. |
|---|---|---|---|---|---|
| Original..... | −1.24 | | | | |
| On 4 mm..... | −1.11 | 49.05 | 49.05 | 43.64 | 43.64 |
| On 8 mesh..... | −1.12 | 26.50 | 75.55 | 23.79 | 67.43 |
| On 14 mesh..... | −1.35 | 15.80 | 91.35 | 17.10 | 84.53 |
| On 20 mesh..... | −1.05 | 4.95 | 96.30 | 4.17 | 88.70 |
| Through 20..... | −3.81 | 3.70 | 100.00 | 11.30 | 100.00 |

This head sample shows that 91.35 per cent. by weight remains on 14-mesh screen and contains 84.53 per cent. of the values.

One part of the sample was ground in a laboratory ball mill for 10 min. using 2-in. balls and a dilution of 75 per cent. solids, with results given in Table 2.

TABLE 2.—*Screen Analysis of Product of Ball Mill Grind*

| | Blende Assay, Per Cent. | Weight, Per Cent. | Cum. Wt., Per Cent. | Value, Per Cent. | Cum. Value Per Cent. |
|---|---|---|---|---|---|
| Original | −1.08 | | | | |
| On 4 mm | −0.20 | 27.60 | 27.60 | 5.17 | 5.17 |
| On 8 mesh | −0.20 | 12.25 | 39.85 | 2.29 | 7.46 |
| On 14 mesh | −0.21 | 10.30 | 50.15 | 2.02 | 9.48 |
| On 28 mesh | −0.48 | 12.40 | 62.55 | 5.57 | 15.05 |
| On 35 mesh | −1.14 | 7.10 | 69.65 | 7.57 | 22.62 |
| On 48 mesh | −1.80 | 4.05 | 73.70 | 6.83 | 29.45 |
| On 65 mesh | −2.43 | 5.00 | 78.70 | 11.38 | 40.83 |
| On 100 | −3.15 | 4.40 | 83.10 | 12.97 | 53.80 |
| On 150 | −3.49 | 4.00 | 87.10 | 13.06 | 66.86 |
| On 200 | −2.88 | 5.70 | 92.80 | 15.35 | 82.21 |
| Through 200 | −2.64 | 7.20 | 100.00 | 17.79 | 100.00 |

After grinding in a ball mill, 50.15 per cent. by weight remained on the 14-mesh screen but carried only 9.48 per cent. of the values.

Several similar tests were made on other parts of this head sample of Barnsdall No. 3 tailing in which the time of grinding and the size of the balls were varied. In all these tests, the over-size remaining on 14-mesh screen weighed from 40 to 65 per cent. and contained from 8 to 20 per cent. of the value. The +14-mesh material assayed from 0.20 per cent. to 0.45 per cent. blende.

Other parts of the same head sample were crushed in rolls. The screen analysis given in Table 3 was made on the product of the one part crushed through rolls set at 7/16-in. opening.

TABLE 3.—*Screen Analysis of Product of Roll Crusher*

| | Blende Assay, Per Cent. | Weight, Per Cent. | Cum. Wt., Per Cent. | Value, Per Cent. | Cum. Value, Per Cent. |
|---|---|---|---|---|---|
| Original | −1.18 | | | | |
| On 4 mm | −0.76 | 30.90 | 30.90 | 20.13 | 20.13 |
| On 8 mesh | −1.23 | 36.70 | 67.60 | 38.70 | 58.83 |
| On 14 mesh | −1.26 | 21.10 | 88.70 | 22.79 | 81.62 |
| On 28 mesh | −1.17 | 7.40 | 96.10 | 7.42 | 89.04 |
| On 35 mesh | −2.80 | 0.40 | 96.50 | 0.96 | 90.00 |
| On 48 mesh | −4.27 | 0.20 | 96.70 | 0.73 | 90.73 |
| On 65 mesh | −3.67 | 0.30 | 97.00 | 0.94 | 91.67 |
| Through 65 | −3.24 | 3.00 | 100.00 | 8.33 | 100.00 |

After crushing in rolls, 88.70 per cent., by weight, remained on the 14-mesh screen and carried 81.62 per cent. of the value.

A comparison of these two products brings out the fact that there has been a reduction of the size of the particles in both cases. However, the most important fact is that the ball mill product shows a marked enrichment in the finer sizes and an impoverishment in the larger sizes, which does not occur in the roll-crushed product. The screen analysis of the ball mill product indicates that a preliminary concentration can be made by a quick grind in a ball mill followed by a screening of the discharge. In this way, about 50 per cent. by weight can be discarded immediately. The roll-crushed product does not give such an enrichment, nor permit such a discard.

When subjected to differential grinding in a ball mill, the soft, porous chats are quickly disintegrated while the other chats have part, or all, of the attached mineral removed by the action of the balls. No attempt will be made to explain just how this action takes place and the reader is referred to the voluminous discussion in the technical literature of the actions taking place in a ball mill. Observation of the product of this type of grinding leads the writers to believe that abrasion plays a large part in causing the enrichment of the finer and the impoverishment of the larger sizes.

A further illustration of the differential grinding principle is contained in the results of analyses of the tailing-mill feed, a roll-crushed product, and of the flotation-plant tailing in which ball mills, using differential grinding, have produced almost all the flotation feed (Table 4).

TABLE 4.—*Analyses of Tailing-mill Feed and Flotation Tailing*

| | Tailing Mill Feed, Per Cent. | Flotation Tailing, Per Cent. |
|---|---|---|
| Silica | −62.76 | 28.56 |
| Alumina | − 0.55 | 0.48 |
| Total iron as ferric oxide | − 3.57 | 2.00 |
| Lime | −10.70 | 22.35 |
| Equivalent to calcium carbonate | −19.10 | 39.86 |
| Magnesia | − 6.27 | 13.53 |
| Equivalent to magnesium carbonate | −13.12 | 28.29 |
| Combined carbonates | −32.22 | 68.18 |

## TAILING-MILL FLOW SHEET

The old Barnsdall No. 3 mill was converted into a tailing mill with the following flow sheet:

The chats are reclaimed by homemade drag-line scrapers. The material from the Barnsdall No. 3 dump goes direct to a bin at the tailing

mill while those from the Acme dump are hauled by railroad to the mill bin. The feed drawn from the bin is elevated to the top of the mill and separated into an oversize and an undersize by a trommel. The oversize drops into a surge bin and is fed from it into a 6 by 4-ft. Colorado Iron Works ball mill equipped with full grate discharge of ⅝-in. openings. The discharge from this mill is screened over Leahy screens with jackets having 3/16-in. round holes. Oversize from these screens goes to discard and the undersize flows to twin elevators.

The undersize from the trommel is deslimed in a drag-belt classifier. Slimes from this classifier go to a thickener. The deslimed sand from the classifier drops into another surge bin from which it is fed to a 6 by 4-ft. Allis-Chalmers ball mill. The discharge from this mill then joins the undersize from the Leahy screens at the twin elevators. After elevating, it is again screened on Leahy screens having ⅛-in. slotted screen jackets. Oversize from these secondary screens is treated on a sand jig (Cooley type), a Bendelari jig (diaphragm type), or returned to the Allis-Chalmers mill, as desired. The undersize from the secondary screens is deslimed in another drag-belt classifier. The slimes go to the thickener. The sand then goes to two 6-cell double-spigot classifiers of a modified Fahrenwald type locally known as the St. Joe classifier. Tabling of this product involves handling a very coarse feed, which makes classification quite important. Roughing tables on unclassified feed were unable to make as low tailing as tables with classified feed.

In the tabling system, the free-mineral middlings are sent to separate tables for cleaning; true or chatty middlings are returned to the ball mills; part of the table concentrates are sent over cleaner tables. Table concentrates vary from 55 to 59 per cent. metallic zinc, with a lime content of from 2 to 3 per cent. Mill conditions can be varied so that more or less of the mineral can be sent to flotation, as desired. Local market conditions controlling the sale of the two kinds of concentrates decides this division.

## Mill Results

Operating results may be illustrated by a typical week, as follows:

| | Assay, Per Cent. Blende |
|---|---|
| *Mill Feed* | |
| Acme dump feed | 2.15 |
| Barnsdall No. 3 dump feed | 2.87 |
| Total feed | 2.44 |
| *Mill Tailings* | |
| Oversize reject | 0.54 |
| Table tailings | 0.61 |
| Jig tailings | 0.67 |
| Flotation tailings | 0.40 |
| Total tailings | 0.55 |

Ball consumption (2½ and 2-in. sizes) has amounted to 0.49 lb. per ton, liner consumption to 0.07 lb. per ton, or a total iron consumption of 0.56 lb. per ton of new feed. Power consumption amounts to 0.39 tons of new feed per horsepower-hour.

## Flotation

As mentioned, the slimes produced in the tailing mill are thickened in a thickener 60 by 14 ft. to about 30 per cent. solids, sampled by a Galigher automatic sampler and pumped 1800 ft. with a Wilfley sand pump to a central flotation plant. This plant was originally designed to treat old mill-pond slimes. It contained three 10-ft. double-spitz K. & K. machines and one 8-ft. single-spitz K. & K. machine for a cleaner. The flow sheet was as follows:

The first two machines were in series and raised iron and some interfering slime. About 0.05 lb. per ton of potassium xanthate and 0.05 lb. per ton of Bogalusa pine oil were added to the first machine for this purpose. The froth, which was discarded, assayed about 15 per cent. iron and 3 to 5 per cent. blende. Without the iron machines in the circuit, the tails were materially higher and a marketable grade of concentrates could not be produced. The zinc was raised in the third machine, to which was added about 0.10 lb. per ton of potassium xanthate, 0.3 lb. of Barrett No. 634, and 0.8 lb. of copper sulfate. The froth produced was recleaned in an 8-ft. K. & K. machine, bringing the grade of concentrates up to 58 to 59 per cent. zinc. The plant handled about 3 tons per hr. The plant was later enlarged to treat all slime feed from the dirt mills, the tailing mill and the slime ponds. It now contains 10 machines: two 10-ft. and one 8-ft. K. &. K. machines and seven 11-ft. Butchart machines. At present the plant receives feed from two dirt mills, the tailing mill and two slime ponds, and averages about 20 tons per hr. A Dorr thickener and surge boxes at the plant assure a steady feed to the flotation machines.

The machines are arranged in three parallel circuits of three machines in series and one cleaner machine. If the feed contains enough iron and interfering slimes to lower the grade of concentrate or raise the tailing assay, the first machine of each series is used to raise the iron and some of the interfering slimes. This is done by adding potassium xanthate, -0.02 lb. per ton; Barrett No. 634, −0.1 lb. per ton; Yarmor steam-distilled pine oil, −0.02 lb. per ton.

Zinc is floated in the second machine, to which is added about 0.44 lb. per ton of copper sulfate and 0.08 lb. per ton of potassium xanthate with enough Yarmor steam-distilled pine oil to build up the froth. The froth, which assays about 57 per cent. zinc and 3 per cent. iron, is sent to the cleaner machine, where it is built up to an average of 60.50 per cent.

Wm R. Chedsey.



zinc and 2 per cent. iron. The froth from the last machine in each series is returned to the first zinc machine.

The amount of iron and interfering slimes in the feed can usually be predicted, as certain stopes in the mine contain much more iron and shaly material (mostly soapstone) than others. The slime ponds also vary in the amount of iron and interfering slimes that they contain. By regulating the mining, both of the underground ore and the slime ponds, the flotation plant can be supplied with a feed containing either much or little iron and interfering slimes, as desired. If the former, the flow sheet is used in which the iron is raised. If the feed contains but little iron and interfering slimes, the flow sheet is changed by raising zinc on all three machines of each series. The froth from the first machine is sent to the cleaner and the froth from the last two machines is returned to the first zinc machine.

When no attempt is made to float the iron ahead of the zinc it has been found that sodium Aerofloat gives slightly better results than xanthate, as the iron content of the concentrates is higher when using xanthate than when sodium Aerofloat is used. This is because sodium Aerofloat does not float pyrite readily in an alkaline circuit. The natural alkalinity of the flotation feed ranges between pH 7.6 to pH 8.2. This is increased to about pH 8.4 by addition of lime.

The reagent consumption when using sodium Aerofloat is as follows:

| Reagent | Lb. per Ton |
|---|---|
| Sodium Aerofloat | 0.057 |
| Copper sulfate | 0.438 |
| Barrett No. 634 | 0.134 |
| Yarmor steam-distilled pine oil | 0.030 |

Since the flotation feed is made up from different sources, it was desirable to know just what results were being obtained from the feed from the tailing mill. To ascertain this, feed was pumped direct to one series of machines and the following results were obtained:

| | Per Cent. |
|---|---|
| Feed | 2.60 blende |
| Tails | 0.40 blende |
| Concentrate | 60.00 zinc (metallic) |

Later, when the dirt mills were shut down for two days and the flotation plant was treating feed from the two slime ponds and the slimes produced from the tailing mill, these results were obtained over the two-day period:

| | Per Cent. |
|---|---|
| Feed | 3.47 blende |
| Tails | 0.74 blende |
| Concentrates | 60.00 metallic zinc |

## Résumé

In laboratory testing to develop a method of treating Waco tailings, it was found that:

1. Gravity methods of concentration were unsuitable on the raw material.

2. Differential grinding in ball mills created an enrichment in the finer sizes and an impoverishment in the larger sizes.

3. Screening of the discharge of the ball mill product allowed a discard of about 50 per cent., by weight, of the coarse material, thus giving a preliminary concentration and avoiding fine grinding of the entire feed.

In the commercial mill built to test out the principles developed in the laboratory, it was found that:

4. Differential grinding in ball mills under operating conditions closely approximated laboratory results.

5. Costs of differential grinding were materially lower than fine grinding costs, because of: (a) large capacity of a given size of ball mill on this type of grind as compared to fine grinding. (Capacity of a 6 by 4-ft. mill is 7 to 10 tons per hr. on fine grinding and 25 to 30 tons per hr. on differential grinding.); (b) low iron consumption per ton treated.

The product resulting from differential grinding gave an oversize, after screening, suitable for immediate discard and an undersize readily amenable to tabling and jigging. The oversize discard was 27 to 32 per cent. of the total tails. In the laboratory tests the discard was taken as +14-mesh material. In the actual operation the discard screen analysis is: 23.5 per cent. on 4 mm. and 41.9 per cent. on 8 mesh. This compares with 27.60 per cent. of +4-mm. or 39.85 per cent. of +8 mesh, as shown in the first table on the results of ball mill grinding. Slimes produced from the tailing mill were quick settling and made excellent flotation feed from which a clean concentrate and a low tailing could be made.

Treatment costs in the milling and flotation steps were lower than the estimates but the reclaiming costs were higher. Total operating costs were within the estimate, as no overhead charges were used in the estimate.

Tonnage samples show that the Colorado Iron Works mill handles about 25 tons per hr. when the tailing mill is treating 50 tons per hr. On the basis of 25 tons per hr. of new feed to each ball mill, the following costs result:

The Allis-Chalmers mill, grinding undersize from the primary trommel and the circulating load of table middlings, costs 11.66 c. per ton.

The Colorado Iron Works mill, doing differential grinding on oversize material from the trommel, costs 4.64 c. per ton.

The total cost of ball milling when the tailing mill is handling 50 tons per hr. of new feed is 8.15 c. per ton.

These costs include labor, power, balls, liners, grates and miscellaneous supplies.

TABLE 5.—*Comparison of Estimated and Actual Operating Expenses*

| Estimated | Rock Ton | Actual | Rock Ton |
|---|---|---|---|
| Reclaiming | $0.035 | Reclaiming and hauling | $0.0711 |
| Total milling | 0.135 | Total milling | 0.108 |
| Flotation | 0.120 | Flotation | 0.0966 |
| Total cost per ton of tailings | $0.29 | Total operating cost per ton of tailings | $0.2757 |
| | | Liability insurance | 0.0052 |
| | | Assaying | 0.0025 |
| | | Underground pumping | 0.0067 |
| | | Fire and tornado insurance | 0.0066 |
| | | General expense | 0.0222 |
| | | Total cost | $0.3189 |

The actual operating expenses were based on treating 243,805 tons of feed in the tailing mill, of which 53,395 tons were sent to the flotation plant as slimes.

## DISCUSSION

L. D. HUNTOON, New York, N. Y.—This paper is especially interesting to me because in 1896 I conducted a series of tests on Cripple Creek ores along the same general lines and recommended the treatment of low-grade Cripple Creek ores by crushing and sizing where a large percentage of the values was highly concentrated in the fines. My detailed notes of the many tests have long since disappeared but a summary of results is contained in Richards' Ore Dressing, page 1566, under the title of Concentration by Crushing and Sizing. Several years later I was called upon to investigate the treatment of the waste rock dump from the Independence mine at Cripple Creek. This dump had been carefully sampled by the sinking of test pits; the final report showed 500,000 tons assaying $4 per ton. Here again I repeated my former investigation in a small test mill at the Independence mine and recommended the concentration of the dump by crushing and sizing. This recommendation was followed and a mill was erected under the management of Philip Argall. Not only was the waste dump successfully treated but the process valorized the low-grade ores in the mine, which would not stand shipping to the mills at Colorado Springs.

While professor of mining and metallurgy at Yale I carried on many such investigations on ores and waste products from metallurgical plants; the results from these tests were most interesting and concentration by crushing and sizing was recommended many times.

In 1908 I first visited the Joplin district and was impressed with the enormous tonnage of tailings throughout the area and the high percentage of blende contained in the tailings. For several years later I was called upon by Joplin operators to examine their mills and make recommendations. In many cases, the recovery was less than 50 per cent. and the losses were in the form of chats and fine blende. My recommendations were to screen out the coarse low-grade tailings and fine high-grade material and to crush and screen the intermediate sizes or chats. These professional

investigations led me to have the large and smaller high-grade tailings dumps sampled with the idea of treating them in a centralized mill along the same general lines as that outlined by Banks and Johnson. Although the mining companies to which I submitted my recommendations at that time would not consider the erection of such a centralized tailings mill, it is a satisfaction to know that the process recommended by me has been introduced and has proved a success.

In the examination of ore deposits of value I always have petrographic analysis made not only for the genesis of deposition but to determine the degree of grinding necessary to liberate the mineral.

F. Tartaron, S. Strafford, Vt. (written discussion).—The authors present statistics to show that, in attempting to make a differential grind on tailings, the ball mill is more efficient in their case than rolls. They use as a basis for comparison the percentage of total value of the ore remaining on a 14-mesh screen. Thus, they state that with a feed that before grinding contains 84.53 per cent. of the total value on 14 mesh, on grinding in the ball mill only 9.48 per cent. of the total value remains on this mesh, whereas, after grinding in rolls, 81.62 per cent. is coarser than 14 mesh. Hence, they conclude, the ball mill is more efficient than the rolls.

A further study of the statistics indicates that this conclusion is not justified. The ball mill has been allowed to grind the ore to a much finer size than the rolls. With the former, 50.15 per cent. is on 14 mesh after grinding, whereas, with the latter, 88.7 per cent. is still on 14 mesh. In other words, the product of the rolls is substantially the same as the feed, given as 91.3 per cent. on 14 mesh and no work has been done on the ore in this case. Consideration of the type of material treated indicates that reduction in size is important. Blende has been observed to be contained in the cells of a porous lime chat which forms part of the ore. It is obvious that liberation of this blende is dependent on the breaking up of these chat particles. Hence, since liberation of values is a function of fineness of grind, it is no wonder that the ball mill shows up better than the rolls.

The ball mill has ground 41 per cent. of the ore through 14 mesh. The values contained in this 41 per cent. serve to enrich the −14-mesh material. With the rolls, only 2.6 per cent. has been ground through 14 mesh. It is to be expected that in the latter case the enrichment of the −14-mesh material is negligible.

The writer believes that the rolls should have been adjusted so as to produce the same liberation of values as the ball mill and then estimates of costs should have been compared. It is possible that a finer grind in rolls would cost less and yet produce the same results as the ball mill, but it seems quite obvious to the writer that if one sample of ore is ground and another is not, the latter will show no change from the original ore, and cannot be compared with the former.

W. H. Coghill, Rolla, Mo. (written discussion*).—This excellent paper is indicative of what research is doing for ore dressing throughout the industry. Differential grinding as employed by these men is only one of several important steps in their milling system, which, in terms of methods employed 10 years ago, are innovations.

In many of the Western camps the tailings ground to flotation size are sluiced down the canyon and forgotten; but in the Tri-State district piles of tailings tower 100 ft. high on level country, and are a continual "teaser" to those seeking profitable investments. So it was that no sooner had tailing piles begun to appear than someone undertook to re-treat them. The first efforts were failures, in part because the art had not been developed sufficiently, and in part because the steps that had been developed had not sufficiently impressed the operator.

* Presented by permission of the Director, U. S. Bureau of Mines.

Although little was done to supply a flotation machine with a feed, this district can boast of being among the first to install one. Not until about 1923 was there concordant action among the operators to make thoroughly deslimed jig tailing by beginning the desliming at the head of the rougher jigs and carrying it consistently through the mill. The first flotation filter was introduced in October, 1924.

The first ball mill was installed about 15 years ago, but it could not function without good flotation practice. Now, although ball mills are often a sort of catch-all for the rest of the plant, testimonials of harmonious working of ball mills, float machines and filters are abundant. These improvements, with others, have functioned with the differential grinding of Messrs. Banks and Johnson to make profitable the treatment of tailings with a tenor between 2 and 3 per cent. blende.

According to J. P. Dunlop,[1] more than 3,500,000 tons of tailings was treated in the Tri-State in 1928. The yield was approximately 18 lb. of zinc per ton of tailings, for which the operator realized about 3 c. per pound, or 54 c. per ton of tailings treated. Out of this the operator had to pay a royalty of about 8 per cent. Fortunately the charges against the investment are moderate because the plant is on the ground and otherwise would have to be salvaged. Operators holding piles better than the average enjoy a good margin of profit.

TABLE 6.—*Comparative Grinding Rates of Mixed Chert and Dolomite in Rolls and in a Ball Mill*

| Size | Mixed Feed to Rolls, Per Cent. | Distribution in Roll Discharge | | Mixed Feed to Ball Mill, Per Cent. | Distribution in Ball Mill Discharge | |
|---|---|---|---|---|---|---|
| | | Chert, Per Cent. | Dolomite, Per Cent. | | Chert, Per Cent. | Dolomite, Per Cent. |
| 0.371 in. | 11.9 | 0.8 | 0.7 | | | |
| 0.371 in. +3 mesh | 46.8 | 6.6 | 7.2 | | | |
| MESH | | | | | | |
| 3 to 4 | 41.3 | 38.4 | 36.8 | | | |
| 4 to 6 | | 24.2 | 22.2 | 43.2 | 26.5 | 11.1 |
| 6 to 8 | | 10.5 | 12.0 | 24.8 | 20.1 | 7.5 |
| 8 to 10 | | 7.0 | 6.3 | 19.7 | 15.4 | 6.2 |
| 10 to 14 | | 4.0 | 3.0 | 12.3 | 11.3 | 4.7 |
| 14 to 20 | | 2.7 | 2.1 | | 7.3 | 4.7 |
| 20 to 28 | | 1.7 | 1.7 | | 4.7 | 5.6 |
| 28 to 35 | | 1.5 | 1.5 | | 3.6 | 7.1 |
| 35 to 48 | | 0.8 | 1.3 | | 3.0 | 8.3 |
| 48 to 65 | | 0.4 | 0.9 | | 1.9 | 6.9 |
| 65 to 100 | | 0.4 | 0.9 | | 1.5 | 6.8 |
| 100 to 150 | | 0.2 | 0.7 | | 1.1 | 5.6 |
| 150 to 200 | | 0.2 | 0.6 | | 0.6 | 3.7 |
| −200 | | 0.6 | 2.1 | | 3.0 | 21.8 |
| Total..... | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | Reduction ratio by mean mesh of chert = 2.03<br>Reduction ratio by mean mesh of dolomite = 2.28 | | | Reduction ratio by mean mesh of chert = 1.73<br>Reduction ratio by mean mesh of dolomite = 6.75 | | |

[1] J. D. Dunlop: Advance report, U. S. Bur. Mines.

In the paper under discussion the writers believe that abrasion plays a part in the differential grinding. Arguments about abrasion, attrition and impact do not seem to have led us to fundamentals. It is known that the amount of grinding in rolls depends primarily on the setting of the rolls, but in ball mills the time element is an important factor because when soft material is ground in a ball mill for the same period as hard material the softer component suffers the greater reduction. The justification for this view comes from a study of the relative grinding rates of dolomite and flint in a synthetic mixture of southeast Missouri dolomite gangue and southwest Missouri chert gangue. When the rolls had a given setting the amount of reduction of the two gangues was about the same, but in the ball mill the dolomite had the higher grinding rate. In the rolls the reduction ratio of the chert was 2.03, and that of the dolomite was 2.28; whereas in the ball mill the reduction ratio of the chert was 1.73, and the reduction ratio of the dolomite mounted to 6.75. The results of the tests are shown in Table 6. Hence rolls are of greater advantage when mixed grains have to be ground to a certain size without sliming any of the constituents, but the ball mill is better when the softer mineral requires maximum grinding. The ultimate results may be determined accurately, but the part that attrition plays is uncertain.

The location of the ores described by Banks and Johnson is outside the geographic limits of the famous Picher zinc district. The Picher ores do not contain mineralized limestone; their gangue is flint, and the mineral is disseminated through the flint. Differential grinding as practiced by Banks and Johnson does not apply to these ores. It was tried several years ago in the U. S. Bureau of Mines laboratory at Rolla, Mo., by C. O. Anderson and Henry Aspoas. They called the method "tumbling"; they visualized about twice the normal feed passing through a ball mill and expected a goodly liberation of the mineral. They thought also that the grains that still contained locked mineral would have shapes more favorable to gravity concentration than formerly. But the mineral did not liberate as freely as anticipated; as much as 33 per cent. of it remained in the part coarser than 10 mesh, which was 54 per cent. of the total weight of the charge. However, this was not proof of insufficient liberation. Such proof was obtained by using heavy solutions to segregate the material lighter than 2.80 sp. gr. The float-and-sink tests showed that when one-half was ground to pass 10 mesh the coarser half would yield a jig tailing assaying 1.0 per cent. blende or more, and would suffer an additional loss in chats that would require regrinding. In the work of Banks and Johnson the screens rejected an oversize of one-half this tenor.

The sample that Anderson and Aspoas examined by the tumbling method had a tenor of 3.1 per cent. blende. It was a sample of the +10-mesh portion of a tailing pile. As the ore had been milled through ½ in., the sample was between ½ in. and 10 mesh. Float-and-sink tests showed that 5.0 per cent. was heavier than 2.80 sp. gr. and assayed 34.0 per cent. blende. Tumbling reduced this amount to 2.85 per cent. with a tenor of

TABLE 7.—*Screen Analysis of Oversize +10 Mesh from Four 1-Min. Grinding Periods*

| Size, Mesh | Weight, Per Cent. | Blende, Assay Per Cent. | Distribution of Mineral |
|---|---|---|---|
| +3 | 17.27 | 1.49 | 13.95 |
| −3 + 4 | 31.61 | 1.87 | 31.89 |
| −4 + 6 | 22.69 | 2.01 | 24.73 |
| −6 + 8 | 16.94 | 1.80 | 16.54 |
| −8 + 10 | 11.49 | 2.07 | 12.89 |
| Composite | 100.00 | 1.85 | 100.00 |

30 per cent. blende. Thus the weight of chats was reduced, but their grade was not much affected. The grade of the +10-mesh sample before and after tumbling was 3.10 per cent. and 1.85 per cent. blende, respectively. The small reduction in grade of the +10-mesh material was disappointing, and the material ground finer than 10 mesh was not rich enough. It had a tenor of 4.53 per cent. blende as compared with 3.10 per cent. for the original sample. The fines were 45.50 per cent. weight and contained only 67.40 per cent. of the mineral. The details of this investigation follow.

The laboratory ball mill was loaded with balls, ½-in. to 10-mesh tailings, and water, then run for one minute, emptied, and screened on 10 mesh. Then the oversize was returned and ground for one minute more and the screening on 10 mesh repeated. This procedure was repeated until four 1-min. grinding periods had elapsed. Thus finally an oversize +10-mesh and four undersize −10-mesh products resulted.

A screen analysis of the oversize +10 mesh resulting from the four 1-min. grinding periods appears in Table 7. The feed was 3.10 per cent. blende, so a reduction in grade to 1.85 per cent. is not great.

Table 8 gives the results of a study of the various sizes of this oversize by means of solutions of high specific gravity. A solution of acetylene tetrabromide with a specific gravity of 2.80 was chosen for fractionating the various sizes.

TABLE 8.—*Float-and-sink Tests of Oversize*

| Size, mesh | Product, Sp. Gr. | Weight, Per Cent. | Blende, Assay Per Cent. | Distribution of Mineral |
|---|---|---|---|---|
| +3 | Float on 2.8 | 97.30 | 0.84 | 54.49 |
| | Sink in 2.8 | 2.70 | 25.08 | 45.51 |
| | Composite | 100.00 | 1.49 | 100.00 |
| −3 + 4 | Float on 2.8 | 97.59 | 1.15 | 60.33 |
| | Sink in 2.8 | 2.41 | 30.55 | 39.67 |
| | Composite | 100.00 | 1.87 | 100.00 |
| −4 + 6 | Float on 2.8 | 96.99 | 1.15 | 55.38 |
| | Sink in 2.8 | 3.01 | 29.79 | 44.62 |
| | Composite | 100.00 | 2.01 | 100.00 |
| −6 + 8 | Float on 2.8 | 97.03 | 0.91 | 48.91 |
| | Sink in 2.8 | 2.97 | 31.01 | 51.09 |
| | Composite | 100.00 | 1.80 | 100.00 |
| −8 + 10 | Float on 2.8 | 96.17 | 0.84 | 38.75 |
| | Sink in 2.8 | 3.83 | 33.14 | 61.25 |
| | Composite | 100.00 | 2.07 | 100.00 |

The mean grade of the floats on 2.8 sp. gr. is about 1.0 per cent. blende. This would be a certain loss if gravity concentration were relied upon.

Table 9 gives the screen analyses of the −10-mesh undersizes removed after each period of grinding.

Each −10-mesh undersize is richer in zinc content than the succeeding ones; the range is from 6.30 per cent. to 2.98 per cent. blende. Also, each size is richer than the same size of the succeeding periods; in other words, the differential grinding effect was most marked at the beginning and gradually failed. This was to be expected, as the differential effect will vanish when all of the original sample has been reduced through 10 mesh. The differential grinding effect is an inverse function of the percentage of weight reduced through the 10 mesh.

A résumé of the five products resulting from grinding—the oversize and the four undersizes—is given in Table 10.

TABLE 9.—*Screen Analyses of 10-mesh Undersize after Each Period of Grinding*

| Undersize Number | Undersize Removed at End of Period | Size, Mesh | Weight, Per Cent. | Blende, Assay Per Cent. | Distribution of Mineral |
|---|---|---|---|---|---|
| 1 | First minute of grinding | −10 + 35 | 59.88 | 3.95 | 37.51 |
| | | −35 + 100 | 17.16 | 9.12 | 24.82 |
| | | −100 | 22.96 | 10.34 | 37.69 |
| | | Composite..... | 100.00 | 6.30 | 100.00 |
| 2 | Second minute of grinding | −10 + 35 | 68.63 | 3.04 | 42.00 |
| | | −35 + 100 | 16.47 | 8.14 | 26.98 |
| | | −100 | 14.90 | 10.34 | 31.02 |
| | | Composite..... | 100.00 | 4.96 | 100.00 |
| 3 | Third minute of grinding | −10 + 35 | 71.07 | 2.50 | 44.59 |
| | | −35 + 100 | 16.89 | 6.15 | 26.05 |
| | | −100 | 12.04 | 9.73 | 29.36 |
| | | Composite..... | 100.00 | 40.0 | 100.00 |
| 4 | Fourth minute of grinding | −10 + 35 | 71.77 | 1.91 | 45.86 |
| | | −35 + 100 | 15.53 | 3.95 | 20.54 |
| | | −100 | 12.70 | 7.90 | 33.60 |
| | | Composite..... | 100.00 | 2.98 | 100.00 |

TABLE 10.—*Composite Analysis of the Five Products from the Tumbling Test*

| Product | Size, Mesh | Weight, Per Cent. | Blende, Assay Per Cent. | Distribution of Mineral |
|---|---|---|---|---|
| Oversize | +3 | 9.41 | 1.49 | 4.55 |
| | −3 + 4 | 17.22 | 1.87 | 10.40 |
| | −4 + 6 | 12.36 | 2.01 | 8.07 |
| | −6 + 8 | 9.23 | 1.80 | 5.40 |
| | −8 + 10 | 6.26 | 2.07 | 4.20 |
| | Total oversize..... | 54.48 | 1.85 | 32.62 |
| Undersize | | | | |
| No. 1 | −10 | 11.28 | 6.30 | 23.07 |
| No. 2 | −10 | 11.48 | 4.96 | 18.48 |
| No. 3 | −10 | 11.59 | 4.00 | 15.02 |
| No. 4 | −10 | 11.17 | 2.98 | 10.81 |
| | Total undersize..... | 45.52 | 4.53 | 67.38 |
| | Composite..... | 100.00 | 3.09 | 100.00 |

This test is one of several. The results did not justify a commercial trial. The conclusion was that differential grinding did not apply effectively enough to ores so disseminated as the Picher ores. The alertness of the authors of the paper under dis-

cussion enabled them to apply differential grinding to an ore like the synthetic one mentioned.

C. E. Locke, Cambridge, Mass.—The old principle, "Save your mineral as soon as you can," I think still exists. The old principle of "Don't grind material that is already sufficiently fine" still exists, and Mr. Dorr has admirably shown how to avoid grinding material that is already sufficiently fine.[2] We might go down through the list of basic principles and find that they exist and apply just as strongly as they ever applied, unless they are modified by metallurgical expendiency. For example, this basic flow sheet may be modified. It is good practice to remove fines that are already sufficiently ground. However, at Kimberley, B.C., they have demonstrated fully to their satisfaction that on the Sullivan ore fine material should pass through their grinding mill before it is classified. In other words, metallurgically it needs a little bit of brightening before it will float satisfactorily; consequently, they will never agree to a desliming operation as their first step of grinding.

J. V. N. Dorr, New York, N. Y.— I think that has been found out in one or two other places.

C. E. Locke.—Banks and Johnson have demonstrated the advantages of differential grinding, taking advantage of the relative hardness and softness of material and utilizing that quality in economically grinding and concentrating their ores. It is the same thing that Mr. Bradley did on the Alaska Juneau—rejecting hard quartz in the grinding and crushing operation. It is the same thing that has been done elsewhere. It is a thing that warrants study everywhere.

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[2] See page 109.

# Importance of Classification in Fine Grinding

By J. V. N. Dorr,* New York, N. Y. and A. D. Marriott,† Denver, Colo.

(San Francisco Meeting, October, 1929)

This paper reviews recent developments in the application of classification practice to the origination of fine-grinding flow sheets and traces the history of the mechanical classifier from its initial application for separating cyanide process sands and slimes down to its present six or more distinctly different applications at copper concentrators; it undertakes to show also, by reference to diagrammatic fine-grinding flow sheets and accompanying operating data from nine copper concentrators in western North America, the advantages gained from improved classificiation flow sheets at these properties in terms of reduced grinding costs, improved flexibility of operation or increased recovery. Comparison is only made between different fine-grinding flow sheets at a given plant and no attempt is made to compare different concentrators, on account of ore variations and differences in metallurgical objectives sought.

The adoption of the flotation process in recent years, and especially the development of selective flotation, has brought a demand for much finer grinding than formerly. This has caused much thought to be given to grinding efficiency, and today there is hardly a mill where the grinding flow sheet is not under close study and subject to frequent changes.

When closed-circuit grinding was introduced into metallurgy some years ago, its value was recognized at once, and since then the combination of mills and classifiers has been regarded and operated as a grinding unit.

Apart from variations in both the grinding and classifying elements of this unit, there have been many variations in grouping tried by different mills to suit varying conditions of ore and plant limitations. Although operators feel that in most cases their present flow sheets are on trial, and the data on present work are often incomplete, we have felt that a discussion of the progress that has been made and an endeavor to show present trends and their results should be of use to the profession. We have therefore prepared flow sheets of some of the larger mills with which we have been in contact and present them with available data as to their results, in the hope that they may be of service now rather than later when practice may have become more standardized and more complete records and analyses have been made. We believe that the data given,

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incomplete as they are, indicate that great progress has been made in the reduction of grinding costs, increased recoveries, and improved plant-operating conditions.

While the title of this paper is broad, the discussion has been confined to wet fine grinding with mechanical classifiers, particularly as carried on in the copper plants of the western part of North America, and has necessarily been limited to the information obtained from contact with the machines with which the authors are familiar; *i. e.*, the Dorr Classifier and Dorr Bowl Classifier.

## Definitions

At the risk of seeming elementary, it has been thought best, for the sake of clarity, to define some of the terms used in the paper.

*Classification* is a mechanical operation which separates the solid constituents of a flowing pulp into two portions according to their respective settling rates. Usually it implies the removal of a finished product, called the "overflow" from a product requiring further grinding, called the "sand."

*Overflow* is the comparatively finer, more slowly settling portion of the original pulp, which is carried over the tail board or lip of the classifier by the flow of water.

*Sand* is the comparatively coarser, more rapidly settling portion of the original pulp which is discharged from the classifier by the mechanical action of the rakes.

*Selective Classification* is classification which has for its object the concentration of the heavy constituent of the original pulp, generally the sulfide, in the sand product, so that it may be ground finer than the lighter portion, generally the gangue.

*Mill* is the generic term used to describe grinding mills, whether ball, pebble, or rod mills.

*Fine grinding* is the reduction of crusher or roll products accomplished by mill-classifier units usually to pass a 14-mesh screen or finer.

*Open-circuit grinding* is a method of comminution which aims to secure the desired reduction in particle size by a single passage of the material through the mill.

*Closed-circuit grinding* is a method of comminution in which a partially finished mill discharge is separated by a classifier into a finished overflow product and an unfinished sand product which is returned to the mill for further grinding.

*Grinding efficiency* has been variously defined and many formulas evolved for its determination. Unfortunately, little agreement is discernible in the results obtained by any two authorities on the subject. From a mechanical standpoint, grinding efficiency should take into account such items as the screen analyses of feed and discharge; tonnage

ground during a given period of time; power, liner and media consumption for that period; maintenance and capital charges, etc. From an economic standpoint, grinding efficiency involves, in addition to the foregoing items, such factors as the recovery of mineral, ratio of concentration, selling price of the metal, etc. Each mill operator attempts to strike a happy medium among the many factors involved—one that will yield him the greatest possible net profit for the flow sheet used—consequently mention of such an ambiguous term in this paper has been avoided as much as possible; instead, where available data permitted, specific factors affecting in no uncertain way the economics and savings in the concentrator itself have been singled out for emphasis.

## Classification

The uses of classification may be grouped under three broad headings:

1. To make a size separation; for example, a sand-slime separation so that each product may be given a different treatment.

2. For closed-circuit grinding, so that the maximum size of particle escaping from the circuit may be limited, and so that the useful work done by the mill may be increased by enabling the mill to operate largely in reducing oversize rather than in overgrinding material already fine enough.

3. For differential grinding of the heavy mineral constituent and the gangue, by selective classification which concentrates the mineral in the sand product and causes it to be ground finer than the gangue before it can escape in the overflow product.

The desired function, together with the character of the ore and such factors as the tonnage to be handled, mesh of separation, etc., determine the selection of the proper size and type of classifier. The Dorr classifier and bowl classifier are in use for making separations from as coarse as 10 mesh to as fine as 350 mesh. The first classifier is better suited for making coarse separations and for handling large circulating loads where relatively small overflow capacity is required. The bowl classifier with the double washing action gives a closer separation at the desired mesh and a cleaner sand product; permits, through the selection of the proper bowl size, any required relation between overflow and sand-raking capacity; offers greater range as a mineral concentrator for selective classification. Finally, it is better suited for separations finer than 48 mesh and for securing an overflow capacity relatively large compared with the sand-raking capacity.

Both machines are capable of adjustment to cover considerable range of conditions. Adjustments in slope of classifier tank, rake speed, and dilution of overflow pulp and, in the case of the bowl classifier, additional adjustments of backwash water and bowl speed, are necessary to obtain the desired closeness and mesh of separation. In designing the

machine, due consideration is given the results desired under specified conditions; final adjustments are made when the particular flow sheet is placed in operation and are varied thereafter as the conditions vary.

## Evolution of Present Fine-grinding Flow Sheets

*Open-circuit Grinding.*—The first application of the mechanical classifier was to open-circuit work with grinding mills in the cyanidation of gold and silver ores, for the purpose of producing two products—a slime-free sand for treatment by percolation and a sand-free slime for treatment by agitation and filtration or decantation.

*Closed-circuit Secondary Mills.*—Advances in the art of treating cyanide slimes and the reduced cost of fine grinding made possible by the early tube mills led to the use of the mechanical classifier as a means of controlling the fineness of the pulp leaving the grinding plant as feed to the all-slime cyanide treatment. Operating in closed circuit with the tube mills, the classifier not only controlled fineness more accurately but greatly reduced grinding costs.

*Closed-circuit Primary Mills.*—The adoption of two-stage fine grinding, due to a recognition that too great a size reduction in one mill with one ball charge was uneconomical, led to the use of the primary mill and subsequently a mechanical classifier in closed circuit with it. Reductions in grinding costs were again obtained, and in addition a convenient means was provided for apportioning the work between the two stages.

*Intermediate Classification between Stages of Fine Grinding.*—The next step was the interposition of a bowl classifier between the primary and secondary grinding circuits. This classifier operated in open circuit, receiving as its feed the overflow from the primary circuit, overflowing material of finished size and discharging a clean sand product direct to the closed-circuited secondary mill. This materially improved operating conditions in varying degree at different plants in accordance with the arrangement of the preceding flow sheet. Some of the principal advantages of the use of this step may be summarized as follows:

1. Because of the additional classifier capacity added, there may be obtained: (1) a lower dilution in the secondary classifier overflow at the same mesh of separation, or a finer separation at the same dilution; (2) an increased circulating load capacity in the secondary circuit caused by feeding the bowl sand directly to the secondary mills.

2. By overflowing the bowl direct to flotation, and thereby causing the primary slime to bypass the secondary circuit, there may be obtained: (1) a greater overflow capacity in the secondary classifiers on account of the reduced tonnage and the absence of primary slime; (2) a more uniform product from the secondary circuit because of the absence of primary slime, which greatly affects classification control.

3. The efficacy of the bowl classifier as a concentrator results in selective classification with concentration of the heavier material in the sand, thus facilitating subsequent differential grinding.

*Finishing Bowl Classifiers.*—Finishing the entire flotation feed in a bowl classifier, with provision for regrinding the sands in a separate or tertiary circuit, first proved attractive in the cyanidation of gold ores in which the values were chiefly associated with the heavy pyrite constituent. Here the bowl reclassified selectively the relatively coarse pulp from the secondary circuit, overflowing the bulk of the quartz and only the finest sulfides for treatment, concentrating the sand product to five or six times the assay of the original ore and regrinding this high-grade material as fine as its assay warranted. The net result has been a higher extraction, a coarser over-all grind, and a reduced grinding cost.

The same principle has been successfully applied more recently in the dressing of copper sulfide ores for flotation. The sulfide mineral, being heavier than the gangue, concentrates readily in the bowl sand, and is subjected to regrinding for more complete liberation of associated minerals. In this way the mill is not burdened with gangue material upon which no further work is required. Moreover, the finishing bowl classifier protects the flotation operation against tramp oversize from preceding classifiers and assures a uniform product from the entire fine-grinding section, convenient for sampling and distribution to the succeeding units.

*Preliminary Desliming Classifier.*—The product from the last stage of crushing generally contains some material of finished size and always a certain amount that is finer than the overflow of the primary classifiers. Accordingly, preliminary classifiers have recently been installed at several plants between the last stage of crushing and the first stage of fine grinding. Operating in this manner, primary slime is removed at the outset and sent direct to flotation (or to subsequent steps in the process) and the effective working capacity of the primary mills is increased.

## Varied Illustrations of Improved Methods of Fine Grinding

Considerable initiative has been displayed by plant operators in applying the fundamental principles involved to a continually closer solution of their respective fine-grinding problems. To give details of the progress at all of the copper sulfide properties in this part of the continent is beyond the scope of this paper. Therefore, the discussion is limited to nine large concentrators selected as representative of the improved methods of fine grinding in vogue.

Each of these plants has remodelled its fine-grinding flow sheet several times during the past few years with striking differences in the results obtained. The changes are shown by the flow sheet diagrams (Figs. 1 to 9) and the results obtained in each case have been indicated, in so far

as available data would permit, in the tabulations and remarks. Some of these flow sheets apply only to test sections rather than to the entire concentrator.

No attempt is made to compare practice at different plants, since the character of the ores and other conditions differ greatly. A comparison of different grinding flow sheets at a given concentrator is justified as long as preliminary crushing and succeeding extraction methods remain fairly constant, and this is the only comparison made in this paper.

### *Indices of Comparison*

The basic figures upon which comparisons are made have been chosen as the best available for definitely indicating present trends. They have been secured or derived in the following manner:

*Rated Section Tonnage* is either the average tonnage handled during a test or the average over an extended normal operating period on which reliable data were available.

*Unit Power Consumption* (kilowatt-hours per ton ground), unless otherwise noted, is the daily section tonnage divided into the daily kilowatt-hour consumption of the fine-grinding section. It usually includes the power consumed not only by the cylindrical mills but also by the classifiers, pumps, conveyors, elevators and other accessories.

*Comparative Screen Analyses* were taken from actual operating records or from reports of tests and represent conditions prevailing when the section was handling its rated section tonnage.

*Metallurgical Results* were obtained in the same manner as the screen analyses. It should be noted that "per cent. Cu" refers to total copper present, regardless of the nature of its occurrence (sulfide, oxide, carbonate, etc.). Consequently, the relative recoveries of available copper (copper sulfide) are masked in these figures.

*Tons Ground per Day through* 100 *Mesh* was derived by multiplying the rated section tonnage by the difference between the percentage of +100 mesh in feed and the percentage of +100 mesh in the flotation heading, both percentages being expressed as decimal fractions.

### *Cananea Consolidated Copper Co., Sonora, Mexico*

The Cananea Consolidated Copper Co.'s mill consists today of three sections, two of which are represented by flow sheet 1 and the third by flow sheet 2 in Fig. 1. These flow sheets and the accompanying comparative operating data were supplied by R. E. Howe, general superintendent, and A. T. Tye, metallurgist. (Tables 1 to 3.)

The increase in section capacity, reduction in unit power consumption for fine grinding, and consumption of grinding media, and the slightly finer over-all grind are of particular interest in this case, because these

improvements were made by increasing the classification capacity and increasing the ball load of the secondary mills from 8 to 15 tons of balls. Part of this improvement may be credited to greater classifier capacity and the remainder to the fact that the ball mills in flow sheet 2 were loaded to capacity whereas the ball mills in flow sheet 1 were underloaded, being handicapped by insufficient driving power.

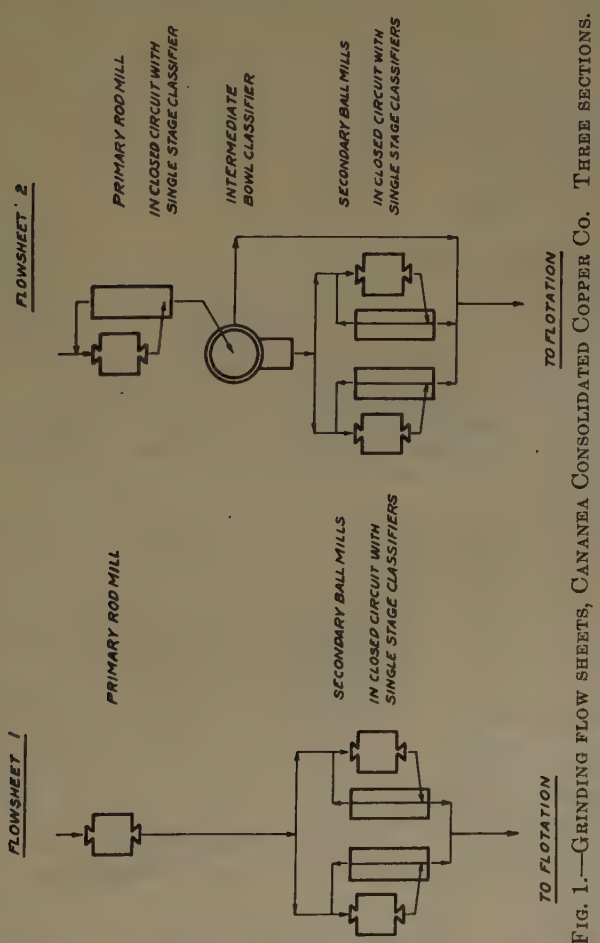



FIG. 1.—GRINDING FLOW SHEETS, CANANEA CONSOLIDATED COPPER CO. THREE SECTIONS.

The advantages of closing the primary circuit have been brought out convincingly by numerous tests, the averages of all of which show that closing the primary circuit has increased 29.2 per cent. the tonnage ground through 48 mesh, equivalent to 105.8 additional tons of −48-mesh product per day, or an estimated saving of $30.68.

The intermediate bowl classifier removes 40 per cent. of the section tonnage which has been finished to flotation heading size in the primary

circuit. The unfinished balance is delivered to the secondary circuit in a deslimed condition and is reground to finished size without difficulty since the ball mills now produce 7.37 tons −48-mesh material per mill

TABLE 1.—*Comparative Capacities and Unit Power Consumptions, Cananea*

6 Months' Average Operation

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Rated section tonnage per day | 707 | 1018 |
| Unit power consumption, kilowatt-hours per ton ground | | |
| Primary mills | 3.05 | 2.20 |
| Secondary mills | 4.93 | 4.32 |
| Classifiers and elevators | 0.34 | 0.18 |
| | 8.32 | 6.70 |
| Unit steel consumption, pounds per ton | | |
| Primary circuit | 0.713 | 0.459 |
| Secondary circuit | 1.328 | 1.283 |
| Total | 2.041 | 1.742 |
| Tons ground per day through 100 mesh | 510 | 798 |
| Unit power consumption, kilowatt-hours per ton −100 mesh | 11.52 | 8.53 |
| Tons ground per day through 200 mesh | 412 | 700 |
| Unit power consumption, kilowatt-hours per ton −200 mesh | 14.30 | 9.73 |

TABLE 2.—*Comparative Screen Analyses, Cananea*

| | Flow Sheet 1 | | | | Flow Sheet 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | +48 Mesh | +65 Mesh | +100 Mesh | −200 Mesh | +48 Mesh | +65 Mesh | +100 Mesh | −200 Mesh |
| Section feed | 82.5 | 86.0 | 89.8 | 5.8 | 87.0 | 89.4 | 92.7 | 4.4 |
| Primary mill discharge | 41.6 | 51.6 | 58.2 | 33.8 | 59.4 | 66.0 | 70.8 | 23.4 |
| Primary classifier overflow | | | | | 42.0 | 49.2 | 55.6 | 36.2 |
| Bowl classifier overflow* | | | | | 1.6 | 4.8 | 10.4 | 78.4 |
| Secondary classifier overflow | 2.0 | 8.6 | 17.4 | 69.0 | 1.1 | 7.2 | 16.5 | 68.6 |
| Combined flotation heading | 2.0 | 8.6 | 17.4 | 69.0 | 1.3 | 6.2 | 14.2 | 73.1 |

* Bowl overflow = 40 per cent. section tonnage.

TABLE 3.—*Comparative Metallurgical Results, Cananea*

6 Months' Average Operation

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Heads, per cent. Cu | 3.52 | 3.39 |
| Concentrates | 22.60 | 21.77 |
| Tails | 0.181 | 0.173 |
| Concentration ratio | 6.70 | 6.72 |
| Recovery | 95.69 | 95.69 |

hour in flow sheet 2 compared with 5.6 tons in flow sheet 1. This increase is due to an increase in ball load and better classification.

*Granby Consolidated Mining, Smelting & Power Co., Ltd., Allenby, B. C.*

The Allenby mill consists of two sections. Flow sheet 1, Fig. 2, represents a fine-grinding section after the addition of finishing bowl

TABLE 4.—*Screen Analysis and Copper Assay Flotation Tailing, Flow Sheet 1, Allenby*

| Mesh | Cumulative Per Cent. Weight | Per Cent. Cu. |
|---|---|---|
| + 65 | 2.70 | 0.66 |
| +100 | 16.34 | 0.45 |
| +150 | 24.58 | 0.39 |
| +200 | 37.88 | 0.38 |
| +270 | 45.08 | 0.26 |
| +325 | 50.40 | 0.23 |
| −325 | 100.00 | 0.17 |

TABLE 5.—*Screen Analysis and Copper Assay Flotation Concentrate, Flow Sheet 2, Allenby*

| Mesh | Before Concentrate Regrind | | After Concentrate Regrind | |
|---|---|---|---|---|
| | Cumulative Per Cent. Weight | Per Cent. Cu | Cumulative Per Cent. Weight | Per Cent. Cu |
| + 65 | 1.76 | 12.28 | | |
| +100 | 10.54 | 11.39 | 0.50 | 17.37 |
| +150 | 16.80 | 12.73 | 1.60 | 20.45 |
| +200 | 27.80 | 14.79 | 4.44 | 19.93 |
| +270 | 38.72 | 17.84 | 9.44 | 19.63 |
| +325 | 46.86 | 23.76 | 18.44 | 21.33 |
| −325 | 100.00 | 36.85 | 100.00 | 35.43 |
| Average..... | | 27.10 | | 32.54 |

TABLE 6.—*Comparative Capacities and Unit Power Consumptions, Allenby*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Rated section tonnage per day..... | 1056 | 1257.4 |
| Tons ground per mill hour..... | 8.8 | 8.7 |
| Tons ground per day through 100 mesh..... | 706 | 987.9 |
| Tons ground per mill hour through 100 mesh..... | 5.88 | 6.85 |
| Tons ground per day through 200 mesh..... | 522 | 824.0 |
| Tons ground per mill hour through 200 mesh..... | 4.35 | 5.72 |

classifiers in 1925. Flow sheet 2, Fig. 2, represents a fine-grinding section as of 1929, with the exception that the intermediate bowl classifier serves

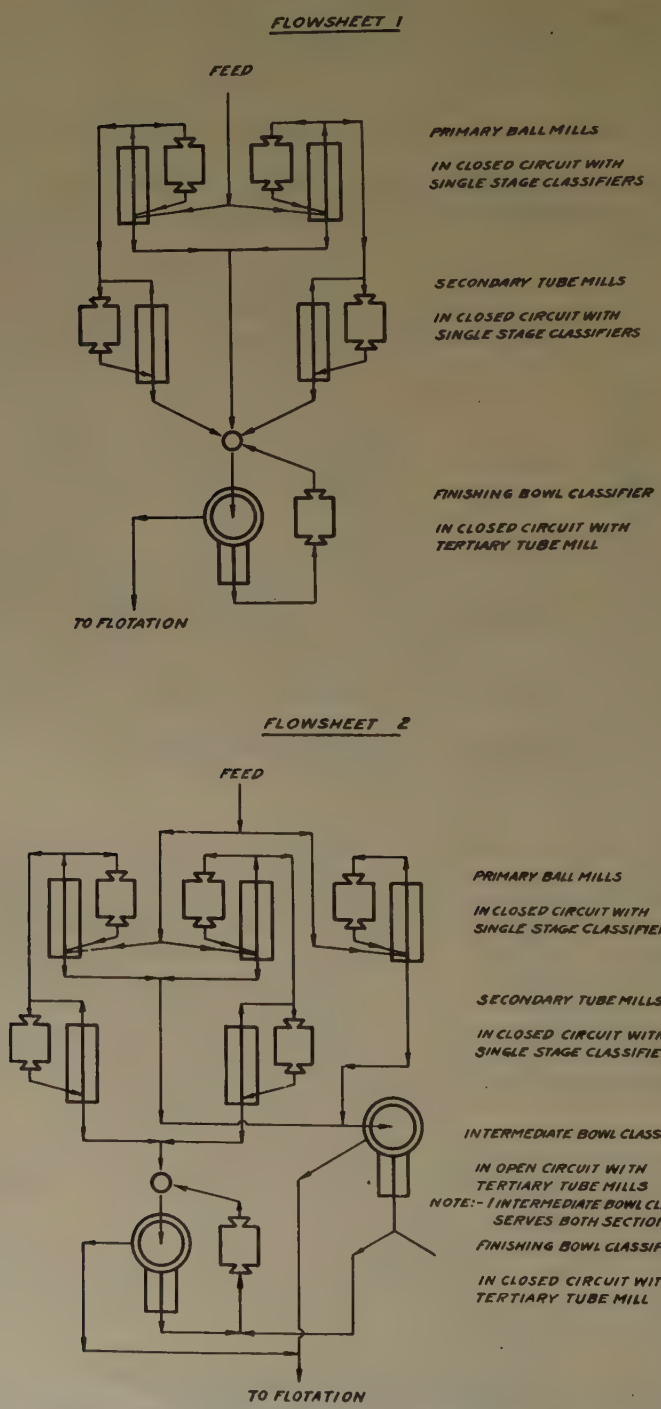



FIG. 2.—GRINDING FLOW SHEETS, GRANBY CONSOLIDATED MINING, SMELTING & POWER CO., LTD. TWO SECTIONS.

TABLE 7.—*Comparative Screen Analyses, Allenby*

| | Flow Sheet 1 | | | | | | Flow Sheet 2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tons | Per Cent. Solids | +48 | +65 | +100 | −200 | Tons | Per Cent. Solids | +48 | +65 | +100 | −200 |
| Section feed | 1056 | | 81.60 | 83.78 | 86.14 | 11.62 | 1257.4 | | 81.60 | 83.78 | 86.14 | 11.62 |
| Primary classifier overflow | 672 | | [b] | 25.24 | 35.27 | 48.40 | 961.1 | 35.8 | 5.57 | 12.77 | 34.74 | 51.43 |
| Intermediate bowl overflow[a] | | | | | | | 797.8 | 30.0 | | | 6.17 | 80.86 |
| Secondary classifier overflow | 384 | | | 25.24 | 35.27 | 48.40 | | | | | | |
| Finishing bowl feed | | 41.8 | | 17.77 | 39.94 | 44.53 | | | 9.33 | 28.83 | 59.56 | 21.44 |
| Finishing bowl overflow | 1056 | 28.0 | | 4.60 | 19.20 | 61.10 | 459.6 | 16.1[c] | | | 10.00 | 70.56 |
| Flotation heading | 1056 | 28.0 | | 4.60 | 19.20 | 61.10 | 1257.4 | 22.8[c] | | | 7.57 | 77.15 |
| Flotation tailing | | | | 2.70 | 13.64 | 62.12 | | | | | | |

[a] Tonnage one-half that actually handled by intermediate bowl which serves both sections.
[b] Screen figures given as combined primary and secondary classifier overflows.
[c] Figures calculated.

TABLE 8.—*Comparative Metallurgical Results, Allenby*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Heads, per cent. Cu | 1.448 | 1.508 |
| Concentrates, per cent. Cu | 27.10 | 32.54 |
| Tails, per cent. Cu | 0.277 | 0.223 |
| Concentration ratio | 22.906 | 25.149 |
| Recovery | 81.705 | 85.80 |

both sections, reclassifying equal portions of primary classifier overflow from each. The flow sheets and the accompanying operating data were supplied by H. C. Smith and H. R. Taylor. (Tables 4 to 8.)

Allenby ore contains as sulfides chalcopyrite and bornite and a very small amount of pyrite. The copper sulfides are finely disseminated throughout the gangue, thus necessitating extremely fine grinding to effect liberation.

The flotation heading produced in flow sheet 1, handling about 100 tons per day, was found to contain too great a percentage of +65 and +100-mesh material, as shown by Table 4, which indicates that the dividing line in the copper lies at 100-mesh separation.

Flow sheet 2 was subsequently adopted for both mill sections. In this manner the +100-mesh material in the flotation heading was reduced by 10 to 15 per cent. and the section tonnage increased from 1000 tons per day to 1250 tons. In the absence of segregated power figures, the two flow sheets are compared on the basis of tons ground per mill hour, which is believed to be roughly inversely proportional to the unit power consumption per ton milled.

A considerably greater percentage of the feed was ground through both 100 mesh (78.6 per cent. as compared with 66.9 per cent.) and 200 mesh (65.5 per cent. as compared with 49.5 per cent.) by means of the additional equipment and its arrangement in flow sheet 2. This is of great importance, because tailing losses were found to mount rapidly in the +200-mesh material, and were relatively even higher in the +100-mesh material.

Shortly after the adoption of flow sheet 2 it became necessary to raise the grade of concentrate, on account of freight charges and smelter rates. Since all the copper in the +200-mesh sizes is attached to gangue, regrinding of the coarse material in the rougher concentrates was decided upon as the most economical method of bettering the grade. The additional equipment provided for this purpose consisted of a thickener, bowl classifier, ball mill and the necessary pumps. Rougher concentrates, after thickening, are reground in the mill in closed circuit with the bowl classifier to a per cent. or two on 200 mesh and refloated and doubly recleaned in a separate circuit. The effect of this change in flotation practice is brought out in Tables 5 to 8.

### *Miami Copper Co., Miami, Arizona*

The Miami Copper Co., as shown by the flow sheets in Fig. 3 and comparative operating data furnished by H. D. Hunt, mill superintendent, and R. L. Montjoy, metallurgist, has gone through four stages of experimentation in the development of fine-grinding flow sheets. Flow sheets 1, 2 and 3 were used at various times from 1923 to 1929, while flow sheet 4 represents the final development as of August,

1929, which, excepting the preliminary classifiers used only in two sections,is now in use in all of the six sections. (Tables 9 to 11.)

Whereas the first flow sheet provided only for closed-circuited secondary mills, the succeeding flow sheets demonstrated the desirability of partly closing the primary circuit, finishing all flotation heading in bowl classifiers, in closed circuit with tertiary regrind mills, and desliming the roll product before introduction into the primaries. All of these features have been incorporated in the final flow sheet 4. The primary circuit would have been completely closed had it not been for insufficient capacity of the classifier overflow.

There has been a progressive stepping up of the tonnage handled per section from 1278 tons per day to 2821 tons per day, and this has been accomplished without a corresponding increase in grinding cost, as evidenced by the unit power consumption of 5.84 kw-hr. per ton in flow sheet 4 as against 6.23, 7.24 and 7.16 in flow sheets 1, 2 and 3 respectively.

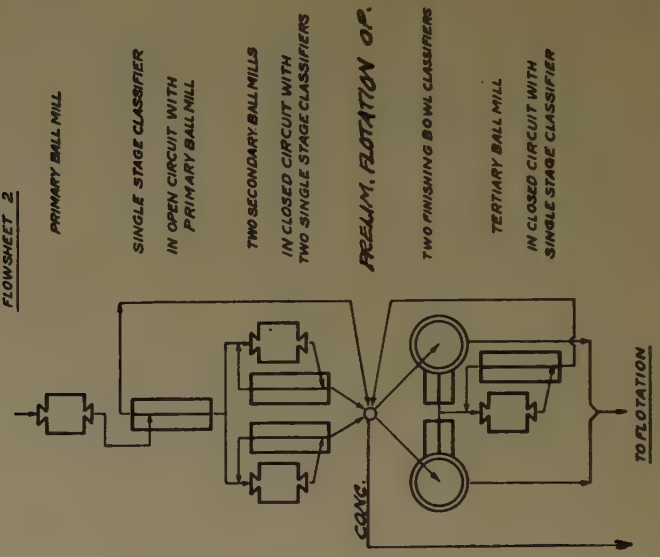
A study of the table of comparative screen analyses (Table 10) shows that the tendency recently has been to grind coarser prior to the first step in flotation, and for this reason the unit power consumption per ton of −100 mesh and −200 mesh does not show the decreases that might be expected. In this connection it should be borne in mind that present practice at Miami calls for a rough concentration of the coarse-grinding section product followed by regrinding this concentrate in a separate circuit prior to final concentration.

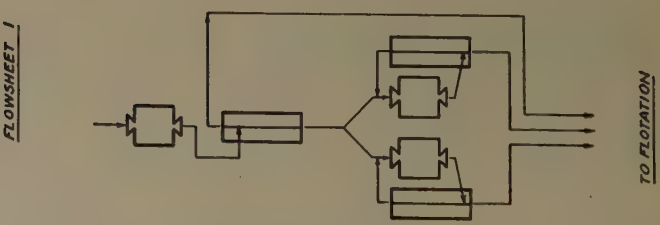
TABLE 9.—*Comparative Capacities and Unit Power Consumptions, Miami*

| | Flow Sheet 1 | Flow Sheet 2 | Flow Sheet 3 | Flow Sheet 4 |
|---|---|---|---|---|
| Rated section tonnage per day | 1278 | 1483 | 1480 | 2821 |
| Unit power consumption, kilowatt-hours per ton milled | 6.23 | 7.24 | 7.16 | 5.84 |
| Tons ground per day through 100 mesh | 804 | 1043 | 969 | 1552 |
| Power consumption, kilowatt-hours per ton −100 mesh | 9.90 | 10.29 | 10.94 | 10.61 |
| Tons ground per day through 200 mesh | 616 | 762 | 721 | 1131 |
| Power consumption, kilowatt-hours per ton −200 mesh | 12.92 | 14.09 | 14.69 | 14.56 |

Where assays are available there is ample evidence of the concentration of mineral in the classifier discharges and the consequent selective grinding action, which subjects the mineral to a finer degree of comminution than the gangue. The density of flotation heading has increased, especially after the introduction of the large finishing bowl classifier in flow sheet 4, overflowing to flotation at 38 per cent. solids.

Miami practice today is an example of three-stage fine grinding with all flotation heading originating at a single point, convenient for


FLOWSHEET 2
PRIMARY BALL MILL
SINGLE STAGE CLASSIFIER
IN OPEN CIRCUIT WITH PRIMARY BALL MILL
TWO SECONDARY BALL MILLS
IN CLOSED CIRCUIT WITH TWO SINGLE STAGE CLASSIFIERS
PRELIM. FLOTATION OF CONC.
TWO FINISHING BOWL CLASSIFIERS
TERTIARY BALL MILL
IN CLOSED CIRCUIT WITH SINGLE STAGE CLASSIFIER
TO FLOTATION


FLOWSHEET 1
PRIMARY BALL MILL
SINGLE STAGE CLASSIFIER
IN OPEN CIRCUIT WITH PRIMARY MILL
TWO SECONDARY BALL MILLS
IN CLOSED CIRCUIT WITH TWO SINGLE STAGE CLASSIFIERS
TO FLOTATION

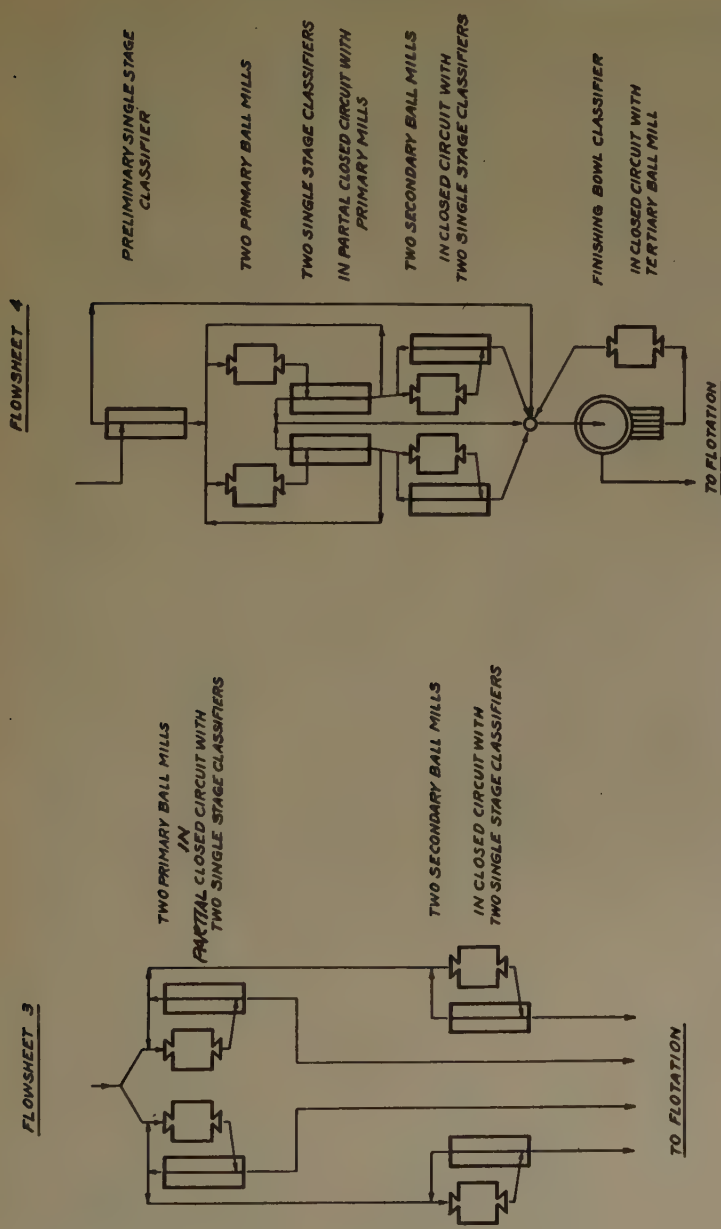



FIG. 3.—GRINDING FLOW SHEETS, MIAMI COPPER CO SIX SECTIONS.

TABLE 10.—*Comparative Screen Analyses, Miami*

| | Flow Sheet 1 | | | | | | | Flow Sheet 2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tons | Per Cent. Cu | Per Cent. Solids | +48 | +65 | +100 | −200 | Tons | Per Cent. Cu | Per Cent. Solids | +48 | +65 | +100 | −200 |
| Section feed | 1278 | 1.81 | 100 | 76.4 | 78.7 | 81.5 | 14.6 | 1483 | 1.64 | 100 | 77.9 | 79.8 | 82.4 | 13.8 |
| Preliminary classifier overflow | | | | | | | | 1483 | 1.64 | 74.7 | 58.3 | 62.7 | 67.7 | 25.4 |
| Primary mill discharge | 1278 | 1.81 | 65.0 | 49.6 | 55.3 | 61.3 | 29.0 | 494 | 1.60 | 39.0 | 8.5 | 15.5 | 25.8 | 59.0 |
| Primary classifier overflow | 472 | 1.60 | 28.1 | 0.8 | 5.0 | 13.6 | 69.3 | 3169 | | 73.5 | 48.2 | 59.4 | 68.6 | 21.2 |
| Secondary mill discharge | 2411 | 2.99 | 70.0 | 33.8 | 49.3 | 62.0 | 24.0 | 989 | 1.73 | 36.0 | 5.8 | 14.6 | 28.6 | 51.8 |
| Secondary classifier overflow | 806 | 1.85 | 35.1 | 1.8 | 8.8 | 22.2 | 55.2 | | | | | | | |
| Finishing bowl classifier feed | | | | | | | | 1483 | | 22.8 | 0 | 2.2 | 12.1 | 65.2 |
| Finishing bowl classifier overflow | | | | | | | | 2022 | 0.77 | 63.4 | 14.0 | 40.8 | 66.5 | 83.2 |
| Regrind mill discharge | | | | | | | | 1142 | 0.56 | 47.3 | 8.8 | 30.1 | 58.8 | 77.4 |
| Regrind classifier overflow | | | | | | | | 1483 | | 22.8 | 0 | 2.2 | 12.1 | 65.2 |
| Flotation heading | 1278 | 1.81 | 33.6 | 1.6 | 7.3 | 18.6 | 62.8 | | | | | | | |

| | Flow Sheet 3 | | | | | | | Flow Sheet 4 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Section feed | 1480 | 1.69 | 100 | 80.9 | 82.9 | 85.2 | 11.6 | 2821 | | 97.0 | 75.6 | 78.4 | 81.8 | 13.7 |
| Preliminary classifier overflow | | | | | | | | 471.1 | | 39.7 | 17.5 | 23.8 | 33.1 | 52.6 |
| Primary mill discharge | 2335 | 1.75 | 71.2 | 52.3 | 60.2 | 67.3 | 23.5 | 3171 | | 65.6 | 62.2 | 67.1 | 73.3 | 19.9 |
| Primary classifier overflow | 623 | 1.55 | 26.7 | 0.3 | 1.8 | 9.0 | 72.0 | 1529 | | 53.9 | 40.5 | 48.5 | 57.2 | 31.7 |
| Secondary mill discharge | 2150 | 2.63 | 69.0 | 32.1 | 48.9 | 62.2 | 24.8 | 1693 | | 63.7 | 39.9 | 50.1 | 60.2 | 27.9 |
| Secondary classifier overflow | 856 | 2.04 | 31.8 | 5.6 | 16.7 | 34.3 | 43.8 | 821 | | 38.8 | 14.1 | 26.0 | 39.2 | 43.2 |
| Finishing bowl classifier feed | | | | | | | | 7404 | | 57.1 | 35.1 | 48.7 | 60.2 | 27.5 |
| Finishing bowl classifier overflow | | | | | | | | 2821 | | 38.0 | 3.9 | 13.2 | 26.8 | 53.8 |
| Regrind mill discharge | | | | | | | | | | 68.9 | 40.5 | 55.3 | 69.9 | 18.6 |
| Regrind classifier overflow | | | | | | | | | | | | | | |
| Flotation heading | 1480 | 1.69 | 29.6 | 2.3 | 7.5 | 19.7 | 60.3 | 2821 | | 38.0 | 3.9 | 13.2 | 26.8 | 53.8 |

adjustment of density and fineness. Ample classifier capacity ahead of and between the various stages with the exception of the under-capacity secondary class fiers, permits finished material to escape quickly as soon as it has received the treatment intended by that particular stage.

*Nevada Consolidated Copper Co., Nevada Mines, McGill, Nevada*

The McGill, Nevada, concentrator of Nevada Consolidated Copper Co., as shown by the six flow sheets of Fig. 4 and accompanying operating data, over a period of years has tested five types of fine-grinding layouts and at the present time is preparing to operate a test section with the

TABLE 11.—*Comparative Metallurgical Results, Miami*

| | Flow Sheet 1 | Flow Sheet 2 | Flow Sheet 3 | Flow Sheet 4 |
|---|---|---|---|---|
| Heads, per cent. Cu | 1.74 | 1.711 | 1.686 | 0.81 |
| Concentrates, per cent. Cu | 42.26 | 47.176 | 39.993 | 38.02 |
| Tails, per cent. Cu | 0.28 | 0.24 | 0.27 | 0.18 |
| Concentration ratio | 28.75 | 31.91 | 28.05 | 60.06 |
| Recovery | 84.4 | 86.3 | 84.5 | 78.1 |

arrangement indicated in flow sheet 6. Flow sheet 1, simple single-stage open-circuit grinding, was used prior to 1919 for preparing ore for gravity concentration; No. 2 was applied in 1919 when flotation was adopted; No. 3 was tried out early in 1928, and Nos. 4 and 5 were subjected to competitive tests in 1929. (Tables 12 to 15.)

There has been a progressive increase in section tonnage without use of additional mills, a reduction in unit power consumption, a reduction in tailing assay and an increase in recovery. Identical grinding and classifying equipment was used in flow sheets 3, 4 and 5 and these three flow sheets were tested simultaneously, yet flow sheet 5, producing the coarsest over-all grind, appeared to give the best metallurgical results.

The conclusions drawn by the metallurgical and operating departments from the comparative tests of flow sheets 3, 4 and 5 are as follows:—

1. Flow sheet 3, where the section heading is sent to the preliminary bowl classifier for the removal of primary slimes ahead of the ball mills, appears to provide for greater section tonnage or finer grinding with the same tonnage, than either flow sheet 4, where the bowl is in parallel closed circuit with the mills, or flow sheet 5, where the bowl is in tandem closed circuit with the mills and single-stage classifiers. This is probably due to the removal of finished material at the outset, thus providing more opportunity for useful reduction of unfinished material in the mills.

2. Flow sheet 5, with the bowl in tandem arrangement, appears to produce conditions in the flotation heading conducive to increased recovery, even though the over-all grind is coarser than that of either

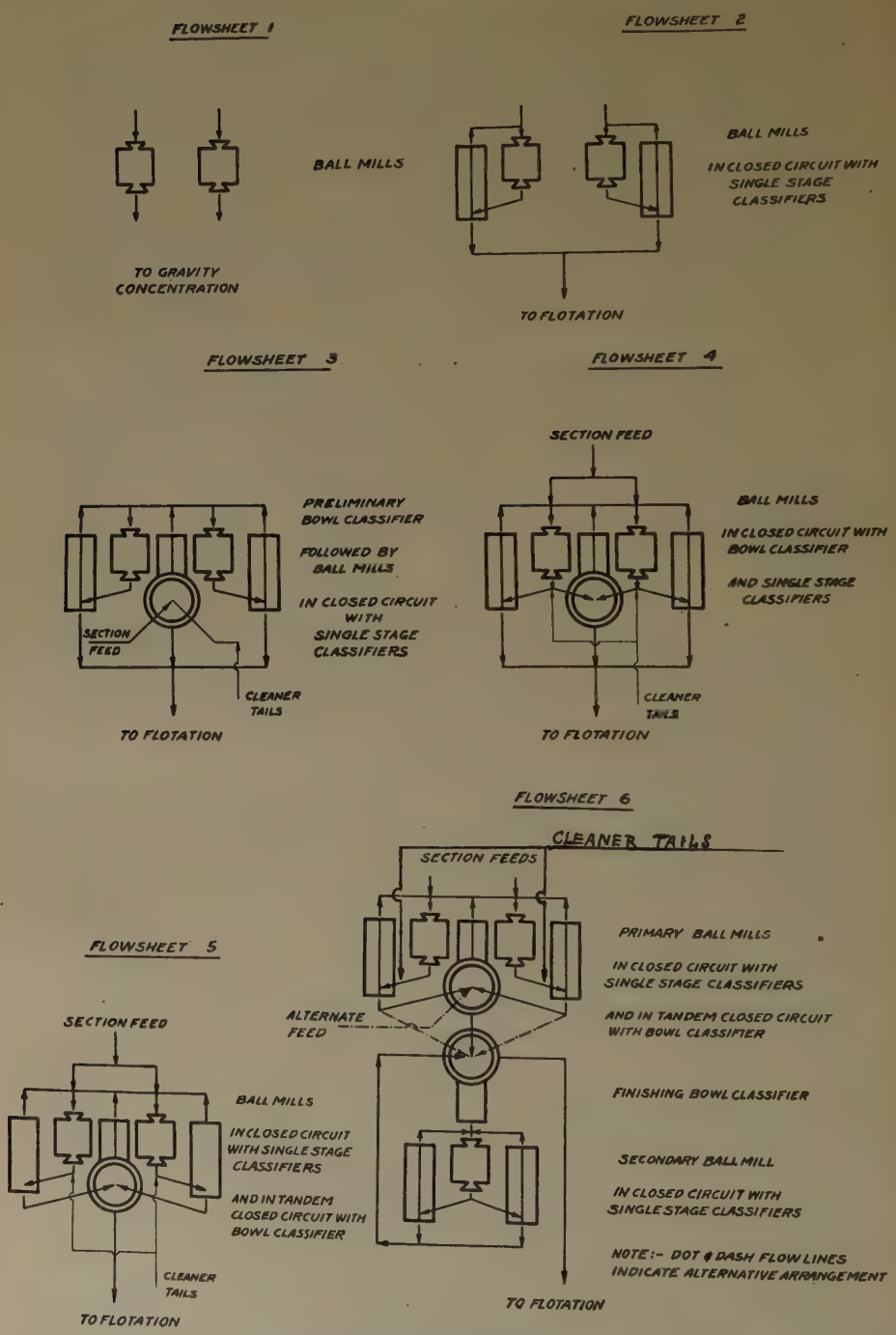



FIG. 4 —HALF-SECTION GRINDING FLOW SHEETS, NEVADA MINES, NEVADA CONSOLIDATED COPPER CO. SIX AND ONE-HALF SECTIONS.

TABLE 12.—*Comparative Capacities and Unit Power Consumptions, Nevada Mines*

| | Flow Sheet 1 | Flow Sheet 2 | Flow Sheet 3 | Flow Sheet 4[b] | Flow Sheet 5 |
|---|---|---|---|---|---|
| Rated section tonnage | 1730 | 2090 | 2910 | 2940 | 2880 |
| Tons ground per mill hour | 18 | 21.8 | 30.3 | 30.6 | 30 |
| Unit power consumption, kilowatt-hours per ton milled[a] | 6.3 | 5.2 | 3.7 | 3.7 | 3.8 |
| Tons ground per day through 100 mesh | 806 | 863 | 1362 | 1329 | 927 |
| Power consumption, kilowatt-hours per ton −100 mesh | 13.5 | 12.6 | 7.9 | 8.2 | 11.7 |
| Tons ground per day through 200 mesh | | 623 | 1004 | 1000 | 706 |
| Power consumption, kilowatt-hours per ton −200 mesh | | 17.4 | 10.8 | 10.9 | 15.4 |

[a] Mills only.

[b] Flow sheet 4 to date has shown to be unfavorable because of difficult operating conditions.

TABLE 13.—*Screen Analyses, Nevada Mines*

PARTIAL COMPARATIVE ANALYSES

| | Flow Sheet 1 | Flow Sheet 2 | Flow Sheet 3 | Flow Sheet 4 | Flow Sheet 5 |
|---|---|---|---|---|---|
| Average section feed | | | | | |
| + 48 | 22.52 | 60.4 | 61.8 | 61.8 | 58.9 |
| + 65 | | 67.2 | 67.8 | 67.8 | 64.0 |
| +100 | 95.2 | 71.8 | 72.8 | 72.8 | 68.6 |
| −200 | | 22.3 | 20.6 | 20.6 | 24.0 |
| Average section tailing | | | | | |
| + 48 | 23.6 | 7.8 | 2.9 | 4.2 | 9.0 |
| + 65 | | 19.9 | 14.0 | 16.7 | 21.8 |
| +100 | 48.6 | 30.5 | 26.0 | 27.6 | 36.4 |
| −200 | | 52.1 | 55.1 | 54.6 | 48.5 |

COMPLETE ANALYSES, FLOW SHEET 5

| | +48 | +65 | +100 | −200 |
|---|---|---|---|---|
| Section feed | 58.9 | 64.0 | 68.6 | 31.4 |
| Ball mill discharge | 42.8 | 57.0 | 67.8 | 32.2 |
| Single-stage classifier overflow | 17.1 | 30.3 | 43.3 | 56.7 |
| Bowl classifier overflow | 6.2 | 14.9 | 26.6 | 73.4 |
| Flotation heading | 6.2 | 14.9 | 26.6 | 73.4 |

flow sheet 3 or 4. The reason for this is presumably the fact that relatively coarse and nonfloatable particles of cleaner tails and even insufficiently ground new sulfides are easily included in the pulp overflowing the single-stage classifiers, but are not readily overflowed from the more efficient bowl classifiers, which, acting as sulfide traps, return the coarse, heavy particles to the ball mills until more complete liberation and selective grinding of mineral has been accomplished.

3. A study of copper losses with flow sheets 3, 4 and 5 indicates the superiority of flow sheet 5, in the case of both the +100-mesh and −100-

TABLE 14.—*Comparative Metallurgical Results, Nevada Mines*
Average of Daily Averages during 16-day Test

| | Flow Sheet 3 | Flow Sheet 4 | Flow Sheet 5 |
|---|---|---|---|
| Heads, per cent. Cu | 1.157 | 1.167 | 1.163 |
| Concentrates, per cent. Cu | 21.67 | 20.78 | 19.78 |
| Tails, per cent. Cu | 0.142 | 0.145 | 0.113 |
| Recovery | 87.94 | 87.93 | 90.27 |
| Concentration ratio | 21.75 | 20.67 | 19.33 |

mesh tailing. Between flow sheets 3 and 4, flow sheet 3 showed a saving in the +100-mesh tailing, due probably to the more efficient operation of the ball mills with a deslimed feed. On the other hand, flow sheet 4 showed a saving in the −100-mesh tailing, probably a result of ball mill treatment of the entire section heading and the consequent cleaning or polishing of the surfaces of the sulfides in the primary slimes.

TABLE 15.—*Daily Loss of Copper in Section Tailing, Nevada Mines*

| | Flow Sheet 3 | Flow Sheet 4 | Flow Sheet 5 |
|---|---|---|---|
| Section tonnage per day | 2880 | 2880 | 2880 |
| Per cent. copper in +100-mesh tailing | 0.178 | 0.207 | 0.152 |
| Per cent. copper in −100-mesh tailing | 0.139 | 0.130 | 0.114 |
| Pounds copper per day in +100-mesh tailing | 3168 | 3925 | 3080 |
| Pounds copper per day in −100-mesh tailing | 5165 | 4462 | 3917 |
| Total pounds copper lost per day | 8333 | 8587 | 6997 |

As a result of these tests the new and improved flow sheet 6 will be experimented with shortly. This flow sheet combines the desirable features of flow sheet 5 with a secondary regrind circuit and an intermediate finishing bowl classifier between stages of grinding. Ample

provision is made for concentration of sulfides in bowl classifiers and their selective regrinding in a separate circuit. As indicated by the dotted lines, preliminary desliming may be employed in order to secure the copper savings in the +100-mesh indicated by the test on flow sheet 3.

A study of the test results in Tables 14 and 15 indicated that even with the coarser grind on flow sheet 5 this arrangement produced the best metallurgy, and a longer test period on the entire plant was established using this flow sheet. During the first 15 days of September, 1929, on the same tonnage per mill, increased grinding has been shown, as is evidenced by the figure for this period of 30.6 per cent. +100 mesh as compared to 36.4 per cent. +100 mesh.

The information and data on Nevada Consolidated Copper Co., Nevada mines, are published through the courtesy of J. C. Kinnear, manager, F. M. Jardine, mill superintendent, and E. H. Mohr, metallurgist.

*Nevada Consolidated Copper Co., Ray Mines, Hayden, Arizona*

At Hayden, as indicated by the flow sheets (Fig. 5) and comparative operating data supplied by W. I. Garms, mill superintendent, and T. H. Oxnam, metallurgist, three different fine-grinding flow sheets have been experimented with in recent years. Flow sheet 2 is now in use in seven of the eight sections, and flow sheet 3 is being studied in the test section in order to establish a basis of comparison between rolls and mills for primary grinding of Ray ore. The test section has not been operating long enough on flow sheet 3 to yield data, so this discussion will be confined exclusively to flow sheets 1 and 2. (Tables 16 to 18.)

The equipment provided in flow sheets 1 and 2 is substantially the same, concentrating tables being used in No. 1 but not in No. 2, and there have been no recent changes in the crushing department. The decided reduction in milling costs, as shown in recent annual reports, has been due to improved methods of operating with existing facilities rather than to any additions or modifications thereof.

The tests that first warranted the fine-grinding flow sheet have been confirmed, and show without a doubt that there is a decided advantage in large circulating loads between mills and classifiers, both due to improved over-all grinding efficiency and to the selective grinding of the minerals. This fact would appear to be borne out by the data which follow. Briefly, practice today with flow sheet 2 compared with earlier practice with flow sheet 1 shows a 16.7 per cent. capacity increase accompanied by a coarser over-all grind (11.2 per cent. +100 mesh against 7.4 per cent. +100 mesh), a reduction in kilowatt-hours per ton from 7.80 to 6.96, a slight reduction in tailing assay, and increase in concentration ratio and decrease in recovery.

The concentration of mineral in the classifier sands is striking and results in highly desirable selective grinding. Whereas in past years the

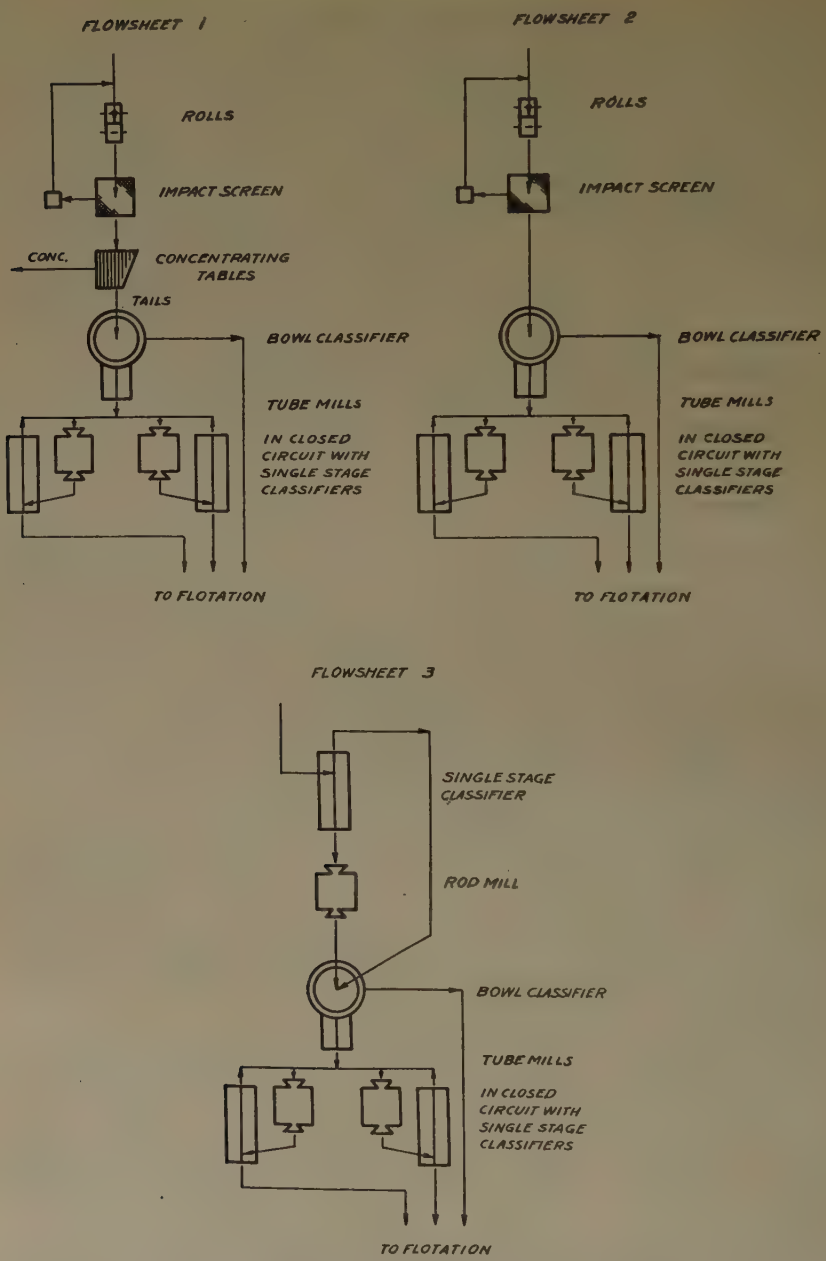



FIG. 5.—GRINDING FLOW SHEETS, RAY MINES, NEVADA CONSOLIDATED COPPER CO. EIGHT SECTIONS.

bowl classifier was operated to produce an all-through 100-mesh product, today the bowl is operated so as to unload at approximately the same mesh as the secondary classifiers, this resulting in a reduction of the feed to the mills and a greater density of overflow to flotation.

Although the flotation heading is considerably coarser than formerly, there is ample evidence that the mineral constituent is receiving the same or even a finer grind. The bowl overflow contains only about one-half as much copper per ton as the sand discharge. While the bowl sand discharge, constituting the feed to the mills, is of a light grayish white color, the sand discharges of the secondary classifiers are decidedly bluish black. This mineral concentration is attributed to the fact that the secondary classifiers now have sufficient raking capacity to allow the mineral load to build up and that the reduced tonnage handled by these classifiers permits classification to take place in clear water, unaided by the buoyant force of the portion of primary slimes formerly introduced at this point. The reduced quantity of bowl-classifier sand now going to the secondary circuit carries almost as much mineral as the former greater tonnage, since now not only the primary slimes are carried off in the bowl overflow, but also a large portion of the barren silica, thus actually producing a classifier sand discharge that is softer and more easily ground in the secondary circuit.

Hayden operation today represents a striking instance of selective grinding of minerals, the providing of ample classifier capacity and the judicious balancing of fine-grinding costs against metallurgical results. Hayden was the first mill to adopt the open-circuit bowl-classifier desliming ahead of ball mills, a practice which has been widely followed elsewhere.

TABLE 16.—*Comparative Capacities and Unit Power Consumptions, Ray Mines*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Rated section tonnage per day | 1500 | 1750 |
| Unit power consumption, kilowatt-hours per ton milled | | |
| Primary circuit (rolls and screens or rod mill and classifier)[a] | 4.01 | 3.38 |
| Tube-mill circuit[b] | 3.79 | 3.58 |
| Total | 7.80 | 6.96 |
| Tons ground per day through 100 mesh | 1200 | 1324 |
| Unit power consumption, kilowatt-hours per ton −100 mesh | 9.75 | 9.20 |
| Tons ground per day through 200 mesh | 988 | 1042 |
| Unit power consumption, kilowatt-hours per ton −200 mesh | 11.84 | 11.69 |

[a] 91.9 per cent. = roll power; 8.1 per cent. = screens and elevators. The wet roll-screen operation to about 10 mesh, while properly a crushing operation, is referred to here as a primary grinding circuit, for the purpose of future comparison.

[b] 90.4 per cent. = tube-mill power; 9.6 per cent. = classifiers and elevators.

TABLE 17.—*Comparative Screen Analyses, Ray Mines*

| | Flow Sheet 1 | | | | | | | Flow Sheet 2 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tons | Per Cent. Solids | Per Cent. Cu | +48 | +65 | +100 | −200 | Tons | Per Cent. Solids | Per Cent. Cu | +48 | +65 | +100 | −200 |
| Section feed | 1500 | 100 | 1.33 | 84.4 | 86.0 | 87.4 | 11.6 | 1750 | 96.5 | 1.29 | 83.96 | 85.2 | 86.86 | 10.85 |
| Preliminary classifier overflow | | | | | | | | | | | | | | |
| Primary circuit product | 1500 | 57 | 1.011 | 31.6 | 37.4 | 43.4 | 48.5 | 1750 | 50.8 | 1.29 | 40.6 | 46.3 | 52.0 | 40.3 |
| Bowl classifier overflow | 725[a] | 20 | 1.037 | 0 | 0 | 0.9 | 91.0 | 700 | 27.4 | 0.84 | | | 5.9 | 82.2 |
| Tube mill discharge | 3000 | | 1.75 | 27.0 | 43.6 | 59.5 | 24.8 | | 76.1 | 2.88 | 25.8 | 39.9 | 58.8 | 22.2 |
| Secondary classifier overflow | 875 | 30 | 0.985 | 0 | 2.2 | 11.7 | 68.6 | 1050 | 33.5 | 1.60 | | 2.1 | 14.8 | 62.6 |
| Flotation heading (calculated) | 1450 | 25 | | | 1.2 | 7.4 | 77.5 | 1750 | | | | 1.4 | 11.2 | 70.4 |

[a] 150 tons returned to secondary classifier.

TABLE 18.—*Comparative Metallurgical Results, Ray Mines*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Heads, per cent. Cu | 1.360 | 1.250 |
| Flotation concentrate, per cent. Cu | 17.664 | 20.246 |
| Gravity concentrate, per cent. Cu | 13.052 | |
| Tails, per cent. Cu | 0.174 | 0.171 |
| Concentration ratio | 13.23 | 18.61 |
| Recovery, per cent | 88.19 | 87.06 |

*Phelps Dodge Corporation, Copper Queen Branch, Bisbee, Arizona*

The two flow sheets (Fig. 6) and comparative operating data on the Copper Queen concentrator, furnished by W. B. Cramer, consulting metallurgical engineer, and E. Wittenau, concentrator superintendent, are representative of practice before the final discontinuation of gravity concentration in 1924 and of practice in 1926 which is still in force. (Tables 19 to 21.)

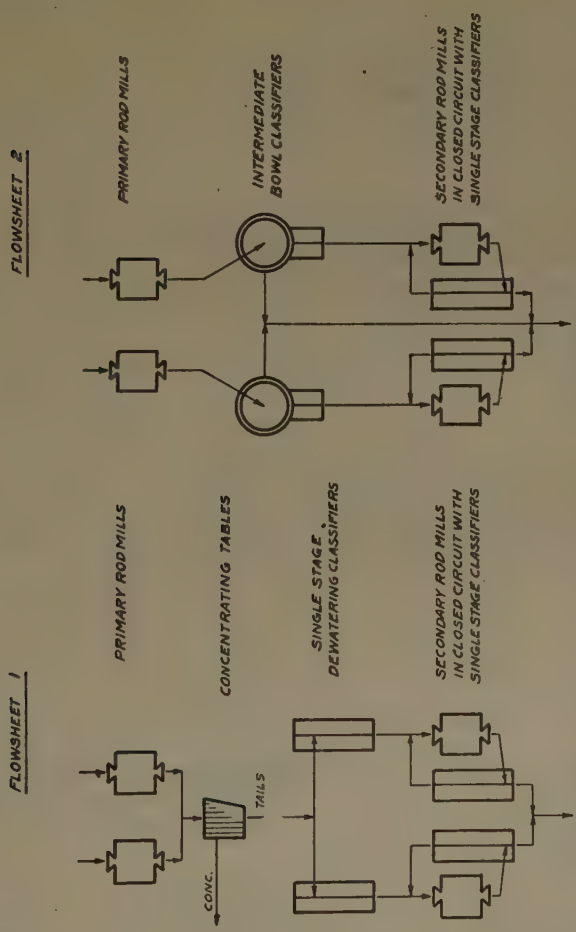



FIG. 6.—GRINDING FLOW SHEETS, COPPER QUEEN BRANCH, PHELPS DODGE CORPN.

The adoption of flow sheet 2 in 1926 was accompanied by a substantial reduction in the tonnage per section, as it was the intention of the management to sacrifice capacity in the interests of much finer grinding and the consequent increase in concentration ratio and reduction in sulfide losses. In Copper Queen ore, copper sulfide and pyrite are closely interassociated, and it was shown that the mineral constituent of the flotation

heading should be ground largely through 200 mesh in order to secure partial selectivity.

The bowl classifiers were accordingly installed between the two stages of grinding in order not only to facilitate finer separations and selective

TABLE 19.—*Comparative Capacities and Unit Power Consumptions, Copper Queen*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Rated section tonnage per day | 1137 | 967 |
| Unit power consumption, kilowatt-hours per ton | 7.47 | 10.13 |
| Unit steel consumption, pound per ton | | |
| Grinding media | 2.29 | 3.02 |
| Mill liners | 0.81 | 0.70 |
| Total | 3.10 | 3.72 |
| Tons ground per day through 100 mesh | 809 | 832 |
| Unit power consumption, kilowatt-hours per ton 100 mesh | 10.49 | 11.93 |
| Tons ground per day through 200 mesh | 550 | 648 |
| Unit power consumption, kilowatt-hours per ton 200 mesh | 15.46 | 15.31 |

TABLE 20.—*Comparative Screen Analyses, Copper Queen*

| | Flow Sheet 1 | | | | Flow Sheet 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | +48 | +65 | +100 | −200 | +48 | +65 | +100 | −200 |
| Section feed | 91.0 | 92.24 | 93.78 | 4.4 | 90.97 | 92.27 | 93.44 | 4.96 |
| Primary mill discharge | 34.1 | 43.94 | 56.04 | 29.29 | 16.24 | 27.14 | 38.37 | 44.29 |
| Bowl classifier overflow[a] | | | | | | | 5.20 | 75.00 |
| Secondary classifier overflow | 3.50 | | 22.64 | 52.76 | | | 9.62 | 68.96 |
| Combined flotation heading | 3.50 | | 22.64 | 52.76 | | | 7.41 | 71.98 |

[a] Bowl classifier overflow = 50 per cent. section tonnage.

TABLE 21.—*Comparative Metallurgical Results, Copper Queen*

| | Flow Sheet 1 | Flow Sheet 2 |
|---|---|---|
| Heads, per cent. Cu | 1.59 | 2.10 |
| Concentrates, per cent. Cu | 6.48 | 15.20 |
| Tails, per cent. Cu | 0.19 | 0.21 |
| Concentration ratio | 4.49 | 7.93 |
| Recovery | 90.71 | 91.26 |

grinding of the mineral but also to act as deslimers, producing a clean sand product with a minimum of finished material for further grinding in the secondary mills. These bowls remove 50 per cent. of finished

flotation heading at a greater density than is possible in single-stage classifiers and thus reduce greatly the tonnage to be handled in the secondary circuit.

The expected improvements in metallurgy have been secured and, according to the officials, are due chiefly to the elimination of gravity processes in favor of all flotation treatment, finer grinding to separate more effectively not only the mineral from the gangue but also the copper constituent from the pyrite, and rearrangement of roughers and recleaners.

*United Verde Copper Co., Clarkdale, Arizona*

The United Verde Copper Co., having recently found from flotation research that a finer grind might prove advantageous in the treatment

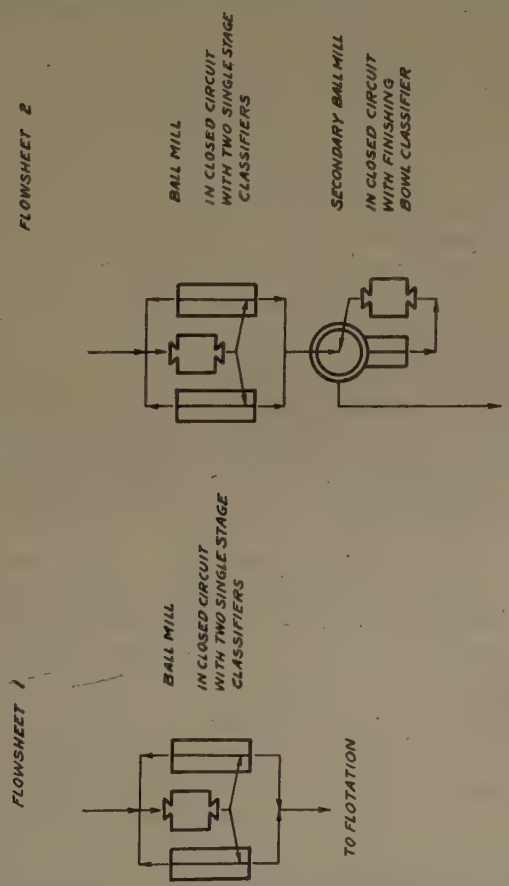



Fig. 7.—Grinding flow sheets, United Verde Copper Co. Two sections.

of schist ores and that a very fine grind was essential to unlock the various minerals in certain massive sulfide ores, installed additional equipment in one of the two fine-grinding sections of the concentrator in order to

TABLE 22.—*Comparative Capacities and Unit Power Consumptions, United Verde*

| | Flow Sheet 1 | Flow Sheet 2 | | | |
|---|---|---|---|---|---|
| Rated section tonnage | 600 | 720 | 800 | 900 | 1000 |
| Mill power consumption, kilowatt-hours | | | | | |
| Primary mills | 4900 | 4900 | 4900 | 4900 | 4900 |
| Secondary mills | | 3300 | 3300 | 3300 | 3300 |
| Total | 4900 | 8200 | 8200 | 8200 | 8200 |
| Unit power consumption, kilowatt-hours per ton milled | 8.16 | 11.4 | 10.3 | 9.11 | 8.2 |
| Tons ground per day through 100 mesh | | | | | |
| Primary mills | 4345 | 395.3 | 476.0 | 445.5 | 423.1 |
| Secondary mills | | 199.4 | 174.4 | 279.8 | 388.0 |
| Total | 4345 | 594.7 | 650.4 | 725.3 | 811.1 |
| Unit power consumption, kilowatt-hours per ton −100 mesh | 11.52 | 14.0 | 12.6 | 11.30 | 10.1 |
| Tons ground per day through 200 mesh | | | | | |
| Primary mills | 343 | 306.7 | 358.8 | 354.2 | 326.1 |
| Secondary mills | | 227.5 | 231.2 | 241 | 299.3 |
| Total | 343 | 534.2 | 590.0 | 595.2 | 625.4 |
| Unit power consumption, kilowatt-hours per ton −200 mesh | 14.28 | 15.35 | 13.9 | 13.8 | 13.1 |

TABLE 23.—*Comparative Partial Screen Analyses Flotation Heading, United Verde*

| | Flow Sheet 1 | Flow Sheet 2 | | | |
|---|---|---|---|---|---|
| Rated section tonnage | 600 | 720 | 800 | 900 | 1000 |
| Flotation heading, per cent. solids | | 18 | 25 | 27 | 28 |
| Flotation heading, per cent. +100 mesh | 17.2 | 2 | 3.5 | 5 | 10.5 |
| Flotation heading, per cent. −200 mesh | 64.7 | 85 | 81.0 | 75 | 69.0 |

TABLE 24.—*Comparative Metallurgical Results, United Verde*

| | Flow Sheet 1 | Flow Sheet 2 | | | |
|---|---|---|---|---|---|
| Rated section tonnage | 600 | 720 | 800 | 900 | 1000 |
| Heads, per cent. Cu | 3.36 | 3.21 | 3.44 | 3.38 | 3.56 |
| Concentrates, per cent. Cu | 16.33 | 17.90 | 17.43 | 15.86 | 16.29 |
| Tails, per cent. Cu | 0.33 | 0.236 | 0.242 | 0.25 | 0.30 |
| Concentration ratio | 5.28 | 5.95 | 5.5 | 4.98 | 4.9 |
| Recovery | 92.04 | 93.8 | 94.2 | 93.9 | 93.2 |

determine the extent to which the extra cost of finer grinding would be repaid in better metallurgy. Flow sheet 1 (Fig. 7) represents the original fine-grinding layout now in use in section 2 while flow sheet 2 is the new

flow sheet in section 1 with provision for finer grinding. These flow sheets and the accompanying data were furnished by Lyle Barker, mill superintendent. (Tables 22 to 24.) From these tests it was concluded that:

1. Two-stage fine grinding is more efficient than single-stage from the standpoint of power consumption, notwithstanding the lack of sufficient classifier capacity in the two-stage flow sheet and an incorrect slope of primary classifiers.

2. Large circulating loads between classifiers and ball mills, 3 to 1 in primary and 5 to 1 in secondary circuit, are essential to maximum output of finished material and correct application of ball sizes.

3. A tonnage of 900 tons per day in the two-stage grinding flow sheet gives the best balance between milling costs and metallurgical improvements. At this tonnage, total milling costs per ton should be slightly less than the corresponding figure for the single-stage flow sheet handling 600 tons per day, while a substantial operating profit should be derived on account of the increased tonnage, lower tailing assay and improved grade of concentrate.

4. At 900 tons of schist ore per day, the two-stage grinding flow sheet may be expected to produce consistently a flotation heading containing 3 to 5 per cent. +100 mesh against 15 to 20 per cent. +100 mesh in the single-stage flow sheet when handling 600 tons per day. When handling massive sulfide ore, a −200-mesh grind may be expected in the two-stage flow sheet when handling 850 tons per day.

### *Utah Copper Co., Salt Lake City, Utah*

Operations at the Arthur and Magna plants of Utah Copper Co. attained in 1927 the figure of 40,000 tons treated per operating day with an average recovery slightly over 89 per cent. During 1928, tonnage increase reached about 50,000 tons per day with somewhat decreased extractions. During the last quarter of 1928, it became economically advantageous to increase to 60,000 tons per day, and in order to meet the conditions of a satisfactory grind with recoveries similar to the 1927 operation, additional equipment was installed in the fine grinding departments. Data on Utah operations are published through the courtesy of D. D. Moffatt, E. W. Englemann, Roy Hatch, T. A. Janney, H. S. Martin, C. G. Williams, L. A. Blackner and A. C. Ensign.

### *Arthur Mill, Utah Copper Co.*

Arthur plant of Utah Copper Co., as shown by the flow sheets 1A and 2A in Fig. 8 and comparative operating data, changed its fine-grinding flow sheet this year from a simple single-stage closed circuit to two-stage grinding with closed-circuit secondary mills, open-circuit primaries and preliminary bowl classifiers for the removal of primary slime of flotation size from the impact screen undersize. (Tables 25 to 27.)

This change in flow sheet was made in order to secure a finer grind prior to flotation in order to increase recovery. The comparative data indicate that with both flow sheets handling substantially the same

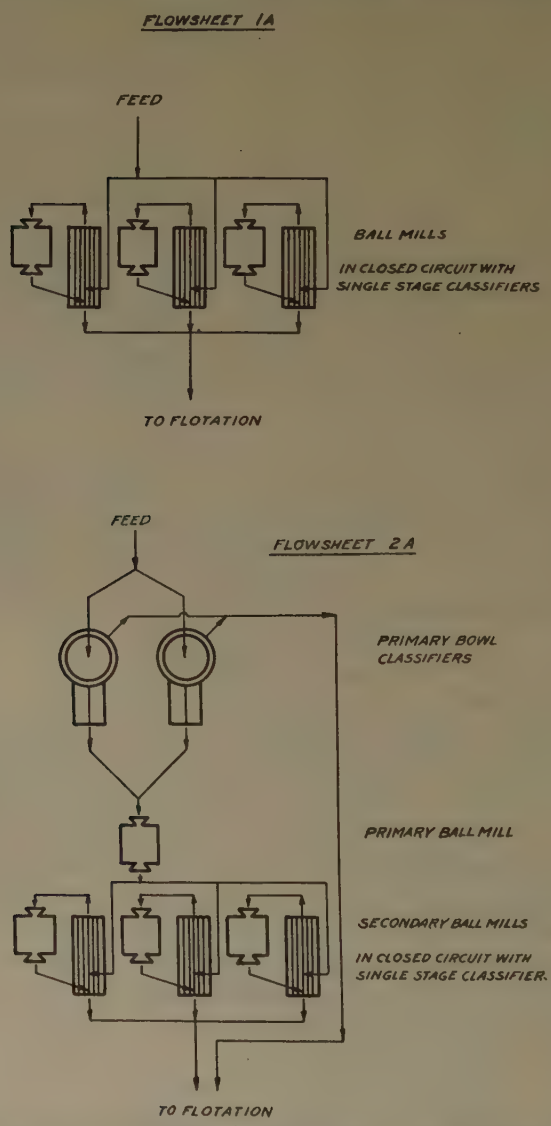



FIG. 8.—GRINDING FLOW SHEETS, ARTHUR MILL, UTAH COPPER CO. THIRTEEN SECTIONS.

tonnage, No. 1A grinding to 26.93 per cent. +100 mesh and No. 2A to 11.73 per cent., flow sheet 2A shows an 0.11 per cent. Cu tailing and an 89.31 per cent. recovery against an 0.188 per cent. Cu tailing and an 81.70

per cent. recovery of flow sheet 1A. This improved metallurgy was obtained at an expenditure of 1.29 additional kilowatt-hours per ton milled, though the power expended in reducing section heading to 100 and 200 mesh was actually less in flow sheet 2A than in flow sheet 1A by 0.92 and 1.41 kw-hr. per ton respectively.

TABLE 25.—*Comparative Capacities and Unit Power Consumptions, Arthur Mill*[a]

| | Flow Sheet 1A | Flow Sheet 2A |
|---|---|---|
| Rated section tonnage per day | 2139 | 2157[c] |
| Unit power consumption, kilowatt-hours per ton milled[b] | 4.39 | 5.68 |
| Tons ground per day through 100 mesh | 806 | 1141 |
| Power consumption kilowatt-hours per ton −100 mesh | 11.66 | 10.74 |
| Tons ground per day through 200 mesh | 580 | 828 |
| Power consumption kilowatt-hours per ton −200 mesh | 16.21 | 14.80 |

[a] Test results not recorded here, show lower power consumption, kilowatt-hours per ton, on greater tonnage operation.

[b] Tube-mill power only, not including classifiers, elevators and accessories.

[c] Tonnage this test held to same value flow sheet 1A to show finer grind.

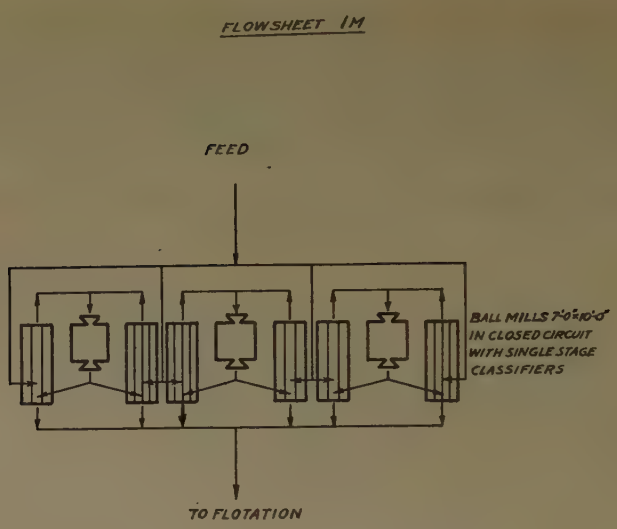
TABLE 26.—*Comparative Screen Analyses, Arthur Mill*

| | Flow Sheet 1A | | | Flow Sheet 2A | | |
|---|---|---|---|---|---|---|
| | Tons | +100 | −200 | Tons | +100 | −200 |
| Section feed | 2139 | 64.63 | 27.35 | 2157 | 64.63 | 27.35 |
| Preliminary bowl classifier overflow | | | | 713 | 5.10 | 81.35 |
| Secondary classifier overflow | 2139 | 26.93 | 54.48 | 1444 | 14.01 | 60.95 |
| Combined flotation heading | 2139 | 26.93 | 54.48 | 2157 | 11.73 | 66.21 |

TABLE 27.—*Comparative Metallurgical Results, Arthur Mill*

| | Flow Sheet 1A | Flow Sheet 2A |
|---|---|---|
| Heads, per cent. Cu | 1.00 | 1.00 |
| Concentrates, per cent. Cu | 31.00 | 32.00 |
| Tails, per cent. Cu | 0.188 | 0.11 |
| Concentration ratio | 37.95 | 35.83 |
| Recovery, per cent | 81.70 | 89.31 |

Tests at Arthur, to determine the effect of finer grinding on recovery of copper, indicate that within the range of grinding with which they are at present concerned (9 to 15 per cent. +100 mesh) each reduction of 1 per cent. in the +100 mesh in the flotation heading is accompanied by approximately 0.004 per cent. Cu reduction in the tailing. Between 3 and 9 per cent. +100 mesh each 1 per cent. reduction in oversize reduces



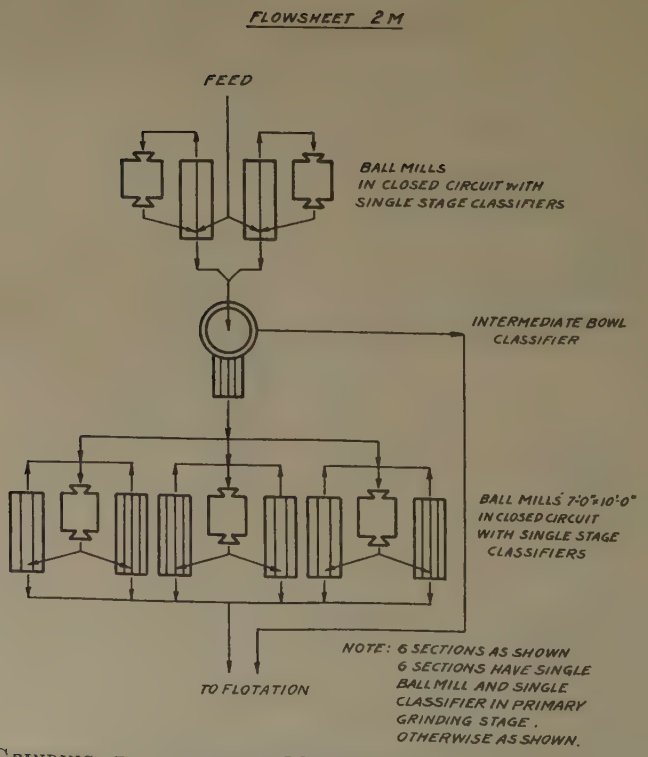




FIG. 9.—GRINDING FLOW SHEETS, MAGNA MILL, UTAH COPPER CO. TWELVE SECTIONS.

the tailing loss about 0.002 per cent. in Cu. A balance between fine-grinding cost and extraction of copper together with pyrite rejection is being investigated with a grind of 1 to 3 per cent. +100 mesh.

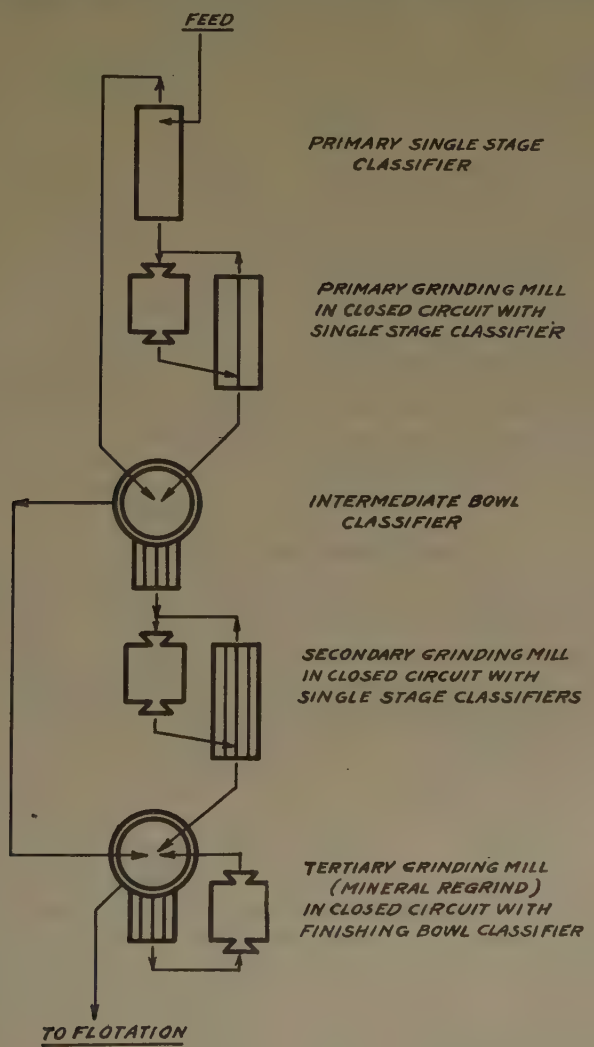



FIG. 10.—SUGGESTED GRINDING FLOW SHEET.

*Magna Mill, Utah Copper Co.*

Magna plant of Utah Copper Co., as indicated by flow sheets 1M and 2M (Fig. 9) and the accompanying data, has just completed the changing of its fine-grinding flow sheet. Where single-stage closed-circuit grinding was practiced heretofore, this concentrator now has two stages of fine grinding, both operating with closed circuits and inter-

mediate bowl classifiers between stages. Six sections have two mills and two single-stage classifiers in the primary circuit and six have only a single mill and a single classifier. The operating figures given are from a section having two primary mills. (Tables 28 to 30)

The old flow sheet 1M when operated at high tonnage naturally produced a coarse flotation heading and gave relatively high tailing and

TABLE 28.—*Comparative Capacities and Unit Power Consumptions, Magna Mill*

| | Flow Sheet 1M | Flow Sheet 2M |
|---|---|---|
| Rated section tonnage per day | 2561 | 2832 |
| Unit power consumption, kilowatt-hours per ton milled[a] | 3.53 | 4.88 |
| Tons ground per day through 100 mesh | 899 | 1546 |
| Unit power consumption, kilowatt-hours per ton −100 mesh | 10.06 | 8.95 |
| Tons ground per day through 200 mesh | 642 | 1186 |
| Unit power consumption, kilowatt-hours per ton −200 mesh | 14.06 | 11.66 |

[a] Tube-mill power only.

TABLE 29.—*Comparative Screen Analyses, Magna Mill*

| | Flow Sheet 1M | | | Flow Sheet 2M | | |
|---|---|---|---|---|---|---|
| | Tons | +100 | −200 | Tons | +100 | −200 |
| Section feed | 2561 | 63.0 | 28.0 | 2832 | 67.7 | 25.2 |
| Primary classifier overflow | | | | | 42.25 | 43.38 |
| Intermediate bowl classifier overflow | | | | | 9.16 | 74.94 |
| Secondary classifier overflow | 2561 | 27.94 | 53.06 | | 16.92 | 57.87 |
| Section flotation heading | 2561 | 27.94 | 53.06 | 2832 | 13.09 | 67.11 |

TABLE 30.—*Comparative Metallurgical Results, Magna Mill*

| | Flow Sheet 1M | Flow Sheet 2M |
|---|---|---|
| Heads, per cent. Cu | 1.00 | 1.00 |
| Concentrates, per cent. Cu | 31.00 | 32.00 |
| Tails, per cent. Cu | 0.188 | 0.11 |
| Concentration ratio | 37.95 | 35.83 |
| Recovery, per cent | 81.70 | 89.31 |

low recovery. At approximately 2500 tons of section feed flow sheet 1M shows a 27.94 per cent. +100-mesh grind, 0.188 per cent. Cu tailing and 81.7 per cent. recovery against corresponding values for flow sheet 2M of 13.09 per cent. +100-mesh, 0.11 per cent. Cu and 89.31 per cent. recovery, with section feed at approximately 2800 tons.

## Summary

The authors' conclusions have been indicated in detail in the remarks accompanying the plant data sections. It is evident from examining these sections that no two properties have developed along quite the same lines, and that no single flow sheet can be said to represent the optimum of present practice. This is inevitable since each concentrator has had its own particular ore-dressing problems, modified by existing plant conditions.

As a means of summarizing the conclusions drawn, however, a generalized flow sheet is attached (Fig. 10) which may be regarded as a composite picture of developments to date. Much thought has been devoted to this flow sheet. It visualizes an arrangement which perhaps might have been adopted in many of these concentrators had local conditions permitted. Data exist to prove the value of each of the steps of this flow sheet at one or more concentrators. There is a probability, of course, that this arrangement will soon be antiquated. It would seem, however, that the composite picture may offer a good basis for such discussion as may follow, and perhaps may serve as a stepping stone for further improvements in fine-grinding practice.

## Acknowledgment

The authors wish to thank the many who have so generously assisted in the preparation of this paper. Several of their own engineers have spared no effort to make it as complete and conclusive as conditions would permit. Particular acknowledgment, however, is due the management and staff of each of the several copper companies mentioned who, by giving unreservedly of the needful data at their disposal, have made the paper possible.

## ADDENDA

Since the presentation of this paper at the San Francisco meeting, the following additional information has become available, which is believed worthy of consideration by metallurgists at this time, especially since it throws additional light on selective classification and the use of the bowl type of classifier as a concentrator of the heavy mineral constituent of the ore to the end that this portion may be more finely ground than the gangue.

At West Springs Mines, Ltd., on the Far East Rand, South Africa, as early as 1920 it was noticed that the refractory gold content of the ore was so encased in a pyritic portion as to necessitate very fine grinding for its release. Shortly after the installation of the first single-stage classifier, it was observed that the small proportion of −200-mesh product in the sand discharge carried abnormally high gold values, thus showing that the classifier had a distinct concentrating effect. After the installation

of bowl classifiers, this observation was confirmed, and laboratory treatment of these values indicated that the gold in the sand product was still mainly locked up or encased in its pyritic envelope and that the product would have to be ground considerably finer to release the bulk of its gold values.

Under existing conditions of cost of tube milling, the economic limit of comminution of the total ore had already been reached. The question, therefore, resolved itself into the further comminution of the pyrite constituent, and this constituent alone. According to a paper[1] on this problem, "Tube milling in two stages, combined with the known concentrating effect of the Dorr bowl classifier, offered a simple means of submitting a selected portion of the total pulp from the primary mills to a further stage of grinding without incurring the heavy expense of bodily abstracting the selected portion from the main pulp stream."

Prior to August 1928, the fine-grinding plant consisted of 10 tube mills in closed circuit with 10 single-stage classifiers, all arranged for a single stage of grinding and for reducing −1½-in. mesh ore to 75 per cent. −200 mesh at the rate of 2000 tons per 24 hr. After August, 1928, two additional tube mills and two bowl classifiers were added so that two-stage grinding might be practiced. In the remodelled plant the ratio of primary to secondary mills could be varied from 10/2 to 9/3, the primaries in each case operating in closed circuit with single-stage classifiers which overflowed to bowl classifiers in closed circuit with the secondaries.

Table 31 gives critical operating data when the grinding plant was operated first with simple single-stage grinding, second with 10 primary and 2 secondary mills, and third with 9 primaries and 3 secondaries. Each set of data represents the average from a three-months' period of continuous operation. These data, in addition to showing a slight increase in capacity and fineness through the adoption of stage grinding, reveal a marked improvement in recovery in spite of the fact that the assay value of the mill heading decreased. The management of the property attributes the increased recovery to the concentrating effect of the bowl classifiers and the finer grinding of the sand discharge from these classifiers in the secondary mills. It will be noted that there has been a very appreciable increase in the gold content of the +90-mesh heading under multiple-stage grinding and a great decrease in the gold content of the +200 and −200-mesh tailings. It was tailing of the latter size which, under former single-stage operation, was largely responsible for the loss of gold encased in a pyritic envelope and resistant to the action of the cyanide solution.

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[1] J. L. Willey and S. E. T. Ewing: Stage Tube-milling and Selective Grinding at West Springs. 1929 Ordinary General Meeting, Chemical, Metallurgical and Mining Society of South Africa.

TABLE 31.—*Critical Operating Data*[a]

| | Single Stage | Two Stage | |
|---|---|---|---|
| Ratio primaries to secondaries | 12/1 | 10/2 | 9/3 |
| Tons milled per tube mill per 24 hr | 200.61 | 210.45 | 206.96 |
| Fineness, per cent. −200-mesh | 77.1 | 79.3 | 81.5 |
| Unit power consumption, kilowatt-hours per ton | 20.6 | 20.3 | 20.5 |
| Unit power consumption, kilowatt-hours per ton −200-mesh | 26.8 | 25.6 | 25.1 |
| Assay value, dollars per ton, heads | 7.122 | 6.346 | 6.168 |
| tails | 0.5116 | 0.399 | 0.358 |
| Theoretical extraction | 92.82 | 93.72 | 94.20 |
| Heads grading assays | | | |
| Dollars per ton +90-mesh | 3.700 | 12.94 | 16.360 |
| Dollars per ton +200-mesh | 2.759 | 2.232 | 2.191 |
| Dollars per ton −200-mesh | 9.064 | 6.966 | 6.552 |
| Tails grading assays | | | |
| Dollars per ton +90-mesh | 0.878 | 0.878 | 0.806 |
| Dollars per ton +200-mesh | 0.775 | 0.475 | 0.393 |
| Dollars per ton −200-mesh | 0.496 | 0.362 | 0.310 |

[a] Gold taken at $20.67 per ounce.

Analyses to determine pyrite content at various points in the fine-grinding department have yielded data to show the extent of concentration (or selective classification) effected, as follows:

| | Original Ore, Per Cent. | Single-stage Classifier Sands, Per Cent. | Bowl Classifier Sands, Per Cent. |
|---|---|---|---|
| Total $Fe_2S$ | 4.4–4.5 | 7.3–7.5 | 8.5–9.0 |
| $Fe_2S$ in −200-mesh | | 17.5 | 36 |

On the basis of these figures, the two-stage fine-grinding plant (10 primaries and 2 secondaries) is superior to the single-stage fine-grinding plant (12 primaries) to the extent of a power saving of 0.3 kw-hr. per ton milled and a $0.1126 per ton recovery of gold formerly lost in the tailing. With average daily capacity 2000 tons, 300 operating days in the year due to week-end shutdowns, and with average power rates of the Electricity Supply Commission of 0.45d ($0.0091) per kw-hr. to the mines on the Rand, the total annual saving, at normal rate of exchange, would be about $69,200.25, of which $67,560 is represented by reduced tailing loss and $1640.25 by reduced unit power consumption.

In like manner the two-stage fine-grinding plant (9 primaries and 3 secondaries) is superior to the single-stage fine-grinding plant (12 primaries) to the extent of a power saving of 0.1 kw-hr. per ton milled

and a $0.1536 per ton recovery of gold formerly lost in the tailing. In this case the total annual saving would be $92,706.75, of which $92,160 is represented by reduced tailing loss and only $546.75 by reduced unit power consumption.

The increase in capacity of approximately 5 per cent., secured without additional mills, presumably has reduced labor, maintenance and overhead charges per ton of ore milled, a factor generally worthy of consideration when capacity is increased by means of simple changes in flow sheet and the replacement of one type of equipment by another. A more detailed discussion of the data presented herein is to be found in the excellent paper on West Springs practice previously referred to in the footnote.

## DISCUSSION

L. M. Barker, Clarkdale, Ariz. (written discussion).—In the creation of the term Selective Classification, the authors, by the use of the adjective, selective, have approached something akin to the compounding of superlatives. The use of such a term, however, is worth while if, as in this case, it emphasizes some condition or set of conditions which have been generally disregarded or overlooked. Not so many years ago, classification was practiced as a fine art as an aid to tabling operations. With the advent of flotation and the necessity for finer grinding, involving as it does the use of mechanical classifiers, it appears that for a time at least certain of the fundamentals of classification have been neglected and forgotten. Recently the millman has awakened to the fact that although the mechanical classifier is different in appearance and operation from the hydraulic classifier of yore the same settling laws are effective in it and the little sulfide particle is found associated with the large gangue particle in the classifier sands. Could anything different be expected and—probably of more importance to certain metallurgists—what steps could be taken to prevent such an occurrence if one were desirous of obtaining a classifier overflow in which the sulfides were no finer than the gangue?

The authors say that the bowl classifier is better suited to the maintenance of selective classifying conditions than the straight classifier, which warrants raising the question as to whether this is not more apparent than real. It is readily recognized that with classifiers operating in closed circuit with a mill the accumulation of sulfides in the circulating load—the classifier sands—might be obscured by oversize gangue so that only chemical analysis would give the true picture of conditions. On the other hand, the sands from a bowl operating in open circuit might, due to the absence of the larger gangue oversize, lead to the impression that the preponderance of sulfides was greater than actually was the case. At the United Verde mill, when operating a unit under flow sheet 2 as outlined in the paper under discussion, analyses of unit products showed the following:

| Product | Sulfides, Per Cent | Gangue, Per Cent. |
|---|---|---|
| Unit feed | 39.34 | 60.66 |
| Primary classifier sands | 54.74 | 45.26 |
| Bowl classifier sands | 53.26 | 46.74 |

The bowl in this case was in closed circuit with the secondary mill and might have been expected to show a greater accumulation of sulfides in the sands than if it had been in open circuit. No flotation reagents were added to the grinding circuit, which

suggests a possible explanation for the efficacy of the bowl as a concentrator in certain mills. It is generally held that the addition of flotation collectors to the grinding circuit permits the overflow of coarse sulfides, of tramp size, from the classifiers presumably through trapping in nascent froth. It is conceivable that the bowl classifier with its greater settling area would permit the settlement of such oversize particles and their return to the mill. Some such explanation is involved in the arguments of the Nevada Consolidated staff at McGill in favor of their flow sheet 5 as against their flow sheet 3, which yielded a finer grind. Unless unusual conditions maintain in a grinding circuit as regards addition of reagents it would appear obvious that, if concentration of sulfides in the sands of both types of classifiers is similar in degree, the finest overflow should yield most readily to subsequent treatment. If such were not the case, study of the problem from the standpoint of pulp conditioning would seem in order.

### Stage Grinding

The generalized flow sheet submitted in the paper certainly depicts the trend of the times but raises many questions as to how to apply it efficiently. Recognizing the advantage of numerous stages in a fine-grinding operation, is it not probable that the addition of stages may be undertaken without a full realization of all the factors involved? As a preliminary to further discussion of this subject the presentation of certain principles is desirable. It is recognized that these principles are not generally acceptable to all millmen, as is demonstrated by the several flow sheets making up this paper, but grouping them as presented below offers food for thought:

1. Mills operated in closed circuit with classifiers are more efficient than mills operated in open circuit.

2. Such increased efficiency probably has its source in the accomplishment of the following things through the circulation of sands: (*a*) reduction of the average size of feed particle; (*b*) increased tonnage fed to the mill as represented by classifier sands; and (*c*), as a consequence of (*b*), rapid removal of finished material from the mill, thus permitting useful work on oversize.

3. The greater the tonnage fed to a mill, whether it be in open or closed circuit, the greater the tonnage of finished material produced.

4. Mill power requirements are but slightly affected by tonnage fed to the mill—the rotation of the mill with its ball load representing the major portion of the power requirements of the system.

5. Efficient utilization of power demands procurement of maximum output of finished material from the mill or jointly from the several mills of a multiple-stage system.

6. On the basis of the foregoing this presumes use of a closed circuit, efficient choice of ball sizes and establishment of proper circulation ratio in the several stages.

7. Use of stage grinding offers opportunities for improved efficiency through correct application of ball sizes to the work to be done.

8. Close sizing of ball charges in the average grinding system is impractical, so that full advantage cannot be taken of principle 7.

With these principles in mind, may we say that, due largely to an inability to closely size ball charges, the efficient use of stages requires stressing of the importance of average size of feed particle to a given stage. That is, inasmuch as sizing of ball charges cannot be held within narrow limits, feed particle size to a given stage cannot be restricted, but rather that the average size of feed particle going to that stage must be brought through the medium of circulation to that which the average size of ball in that stage can reduce most readily. It goes without saying that in a multiple-stage system failure to fully utilize the power input to the several mills—which is constant—could result in an increased power consumption per unit of reduction accomplished

as compared with a single-stage operation efficiently conducted. Fortunately, any addition of stage-grinding equipment in an operation permits an immediate increase in tonnage and the benefits derived in the shape of greater work done on such tonnage may result in a favorable power balance. But is it not probable that the primary stages of this equipment may be operating inefficiently when judged by single-stage standards? May it then be said that in some instances by "backtracking" and checking the work done by the primary stages the addition of a tertiary stage, for example, may be found unwarranted? Is it not often the case that equipment designed for single-stage work is thrown into the position of a primary stage in a two-stage grinding circuit with but minor changes in classifying equipment—quite often reduction—and no other changes but one of ball size? In such a case, what has happened to the average size of feed particle in that stage by virtue of the decreased circulation ratio following the increase in tonnage? A rising power consumption per unit of reduction accomplished following an increase in stages is most certainly indicative of inefficiency and means that some mills are turning over which are not paying their keep. Again, given two flow sheets differing only in number of classifiers and their allocation to the different stages, which when treating the same character of feed show a power balance in favor of that flow using the greater number of classifiers in closed circuit in the several stages, may the conclusion be drawn that average size of feed particle and its relation to average ball size in a given stage was the important factor in such a desirable power balance? The need for greater circulation in the several stages of a multiple-stage grinding system is adequately shown by the paper. However, the desirability of a closer analysis of grinding conditions in the several stages is also evident, and such an analysis might, in many cases, lead to an elimination or consolidation of stages. The number of stages utilized in any case should be determined by the over-all reduction desired and the practicability of suiting ball sizes in each stage to the average size of feed particle sent to that stage.

D. Dyrenforth, Denver, Colo. and C. K. McArthur, El Paso, Texas (written discussion).—The suggested grinding flow sheet is presented as a possible combination of various developments that have taken place during the past year or two at different plants. It is in no wise considered as the ultimate for all fine-grinding operations, but is suggested as a basis for discussion and as an arrangement that may have general application to the larger-tonnage operations. It is believed, therefore, that an analysis showing wherein the data appear to support the various steps of the flow sheet will be of interest.

### Preliminary Classifier

In flow sheets 3 and 4 of the Miami Copper Co., there appear to be several ways in which comparisons may be made. Since we would expect the preliminary classification to benefit only the primary circuit by elimination of the finer sizes in the original feed, it would seem logical to compute the reduction made by comparing the amount of plus in the section feed with the amount in all products passing on to grinding beyond the primary circuit, including both the preliminary and primary classifier overflows going to the third grinding circuit and one-half the primary sand passing to the secondary mills.

In this comparison we find that No. 4 produced about 20 per cent. more through 48 mesh, 15.5 per cent. more through 65 mesh, 13 per cent. more through 100 mesh, and 26.5 per cent. more through 200 mesh. If we compare the actual original feeds to the mills (ore from bins in No. 3 and preliminary classifier sands in No. 4) with primary classifier overflow plus one-half primary classifier sands, we find that the reduction actually in the primary mills with their respective closed-circuit classifiers is 18 per cent. more through 48 mesh, 12.5 per cent. more through 65 mesh, 8.5 per cent. more through 100 mesh, and 18 per cent. more through 200 mesh.

Since, however, both the primary classifier overflow and sand product in flow sheet 4 are coarser than in flow sheet 3, there may be a question as to whether the primary circuit is not by-passing unground material at the expense of secondary circuit. Comparison of the original feeds to primary mills and overflows of primary and secondary classifiers shows that there is in the combined primary and secondary circuits of No. 4 an increased reduction amounting to 17 per cent. more through 48 mesh, 1 per cent. more through 65 mesh, 7 per cent. more through 100 mesh, and 5 per cent. more through 200 mesh.

It is also worth noting that the increased grinding, as shown, is accomplished with less power by 2¼ kw-hr. per ton based on actual tonnage of feed to the primary circuit, which does not in the case of flow sheet 4 include that tonnage overflowed by the preliminary classifier.

At Nevada mines, in flow sheet 3, a bowl classifier operates as a preliminary deslimer. A comparison of this with flow sheet 2 shows increased reductions of the various meshes ranging from about 56 per cent. through 48 mesh to 61 per cent. through 200 mesh. Without doubt, a portion of this increase is due to additional classification and not to elimination of finished material from the mill feed. An indication of the relative amount that may be credited to preliminary desliming is shown by comparing No. 3 with No. 5, where the same bowl classifier is operated in tandem closed circuit instead of as a preliminary deslimer. This comparison shows increased grinding of about 16 per cent. through 48 mesh, 29 per cent. through 65 mesh, 47 per cent. through 100 mesh, and 42 per cent. through 200 mesh. These increases should be discounted slightly, as the screen analyses of section tailings are not truly representative of the grinding because of the circulation of a middling product between classifiers and flotation cells.

The kilowatt-hours on No. 3 are about 28 per cent. less per ton milled, 37 per cent. less per ton ground through 100 mesh, and 38 per cent. less per ton ground through 200 mesh than on No. 2, and as between No. 3 and No. 5, flow sheet 3 shows 3 per cent. fewer kilowatt-hours per ton milled, 32.5 per cent. less power per ton ground through 100 mesh, and 30 per cent. less power per ton ground through 200 mesh.

### Closed-circuit Primary Mill

The work at Cananea affords excellent opportunity to show the advantage of closed-circuit primary operation, as all conditions of primary grinding are the same in the two arrangements except the closed-circuit operation in flow sheet 2. Based on the screen analyses given, the increased reduction in flow sheet 2 amounts to about 58 per cent. more through 48 mesh, 68 per cent. more through 65 mesh, 54.5 per cent. more through 100 mesh, and 63 per cent. more through 200 mesh, with a reduction of power amounting to about 28 per cent. in kilowatt-hours per ton milled and a reduction in steel consumption of about 36 per cent.

At Miami Copper Co., comparing primary mills on flow sheet 2 with primary mills of flow sheet 3, taking one-half the section tonnage in No. 3, we find that the reduction in No. 3 primary is greater than in No. 2 by about 10 per cent. of the 48-mesh size, 24 per cent. of the 65-mesh size, 12 per cent. of the 100-mesh size, and 9.5 per cent. of the 200-mesh size, and this increase is obtained with only partial closed-circuit operation.

### Intermediate Bowl

Considering the rapid adoption of the bowl classifier for open-circuit operation between primary and secondary grinding circuits, it is surprising that its use appears to be very largely an operating convenience. At least, there has not been opportunity to obtain concrete evidence of improved grinding efficiency or improved metallurgy, and it is perhaps for this reason that our own engineers, who have been in close touch

with recent classifier developments, are not entirely in agreement on the use of the intermediate bowl, some being of the opinion that equally good results will be obtained if this additional classification is used for closed-circuit operation with the secondary mills.

The fact remains, however, that the bowl operating as a deslimer between stages of grinding is in successful use at a number of important concentrators, and at these plants both the shift operators and operating officials are as a rule strongly in favor of the use of the bowl in this manner. In addition to the advantages given in the paper under discussion, its use as an intermediate deslimer provides flexibility of mill operation, and an expansion joint, as it were, to take up fluctuations in tonnage, dilution and character of ore, resulting in steadier conditions, particularly in the secondary grinding circuit.

### Secondary Closed Circuit

The importance of closed-circuit operation of the secondary mill requires no advocate today. Every plant discussed is arranged in this manner, and it would be difficult to find any flotation concentrator of consequence where stage grinding is used which has not operated in this manner for the past several years.

The best ratio of circulating load, which determines the amount of classifier sand-raking capacity that should be provided, has been the subject of considerable discussion during the past couple of years. No comment on this will be made here other than to say that there is a definite trend toward greater circulating loads, and it is believed that ratios of from 5/1 to 10/1 will, within the next few years, become as general as the present more or less accepted standard of about 3/1.

### Finishing Bowl Classifier

Reference has been made to the bowl classifier as a machine well adapted to the concentration of the sulfide mineral. There is little concrete evidence from flotation at present to support the contention that the bowl is better for this work than the single-stage classifier. However, combined with such other advantages as unit control of the finished product, proportionately greater overflow, capacity where the sand-raking requirements are relatively less, and finer overflow at greater density, its use in this position seems fully justified.

At Nevada mines, flow sheet 5, with a finishing bowl classifier operating in tandem closed circuit, showed the best subsequent extraction, even though it produced a coarser flotation heading, and this is credited to selective classification of the sulfide mineral.

On Miami's No. 4 flow sheet, mesh assays (Table 32) of the sand and overflow products of the finishing bowl show a decided concentration of copper in that material of the sand products −65 mesh.

Table 32.—*Screen Analysis with Mesh Assays, Miami Copper Co.*

| Mesh | +20 | +28 | +35 | +48 | +65 | +100 | +150 | +200 | −200 |
|---|---|---|---|---|---|---|---|---|---|
| Sand | | | | | | | | | |
| Wt., per cent | 5.0 | 8.2 | 17.1 | 24.3 | 14.4 | 12.5 | 4.8 | 3.0 | 10.7 |
| Cu., per cent | 0.34 | 0.36 | 0.36 | 0.48 | 0.68 | 1.00 | 1.29 | 1.50 | 0.97 |
| Overflow | | | | | | | | | |
| Wt., per cent | | | | 3.9 | 9.3 | 13.6 | 9.5 | 9.9 | 53.8 |
| Cu., per cent | | | | 0.40 | 0.51 | 0.68 | 0.89 | 0.95 | 0.89 |

Of the total copper in the sand product, a little over 65 per cent. is in the meshes finer than 48, and this copper alone is about 24 per cent. of the total copper in the bowl classifier feed.

At McIntyre Porcupine, Schumacher, Ont., the original flow sheet of open-circuit primary mill and closed-circuit secondary mill gave a finished product of 93 per cent. −200 mesh, with a tailing of $0.55 per ton. Selective classification was provided by the addition of a bowl classifier operating in tandem closed circuit with a third mill and single-stage classifier. Table 33 shows a seven-day test, giving the concentration of mineral in this regrinding circuit.

TABLE 33.—*McIntyre-Porcupine Gold Mines, Ltd., Seven-day Test*

| | +200 Mesh, Per Cent. | Assay Value | Pyrite ($FeS_2$), Per Cent. |
|---|---|---|---|
| Bowl Classifier | | | |
| Feed | 61.3 | 6.79 | 7.84 |
| Overflow | 85.6 | 4.49 | 7.59 |
| Sands | 24.7 | 15.40 | 15.71 |
| Circulating Classifier | | | |
| Feed | 39.1 | 19.78 | 20.22 |
| Overflow | 53.7 | 9.56 | 14.79 |
| Sands | 19.0 | 38.57 | 30.93 |

With this coarser over-all grind, a tailing of $0.404 was produced as a result of the finer grind on the pyrite content.

It goes without saying that there will undoubtedly be further developments in classification in fine-grinding operations in the near future. The marked progress of the past year suggests interesting developments for the ensuing period.

A. D. MARRIOTT (written discussion).—Mr. Barker brings up several points of general interest. The term "selective classification" is relative in both single-stage and bowl-type classifiers. Adjustments may be made to produce greater or less selection between minerals of fairly wide specific gravity difference.

It is true that the little sulfide particle is found associated with the large gangue particles in mechanical classifier sands. One would not expect anything else, except, perhaps, as to degree. This is considered an advantage in the vast majority of cases, for the reason that a particle size reduction usually is not to the point of complete liberation either of gangue and sulfide or of valuable and valueless sulfides. There is, therefore, the desire to grind selectively the portion of the ore that requires relatively finer grinding than the average for valuable mineral liberation. In those relatively few cases where it is not desired to have the sulfide finer than the gangue in the pulp as released from the fine-grinding operation to the step that follows in the metallurgical operation, it is necessary to change operating conditions in order to approximate the desired results. If, for best metallurgy, finer grinding of sulfide than the average must be maintained at an absolute minimum, inclusion of some concentration operation in the classifier-mill circuit would seem necessary. Some control is possible, however, by adjustment of the closed-circuit classifier itself.

Mr. Barker has also raised the question as to whether or not the bowl classifier is actually better suited to selective classifying conditions than the single-stage classifier. As Mr. Dyrenforth and Mr. McArthur say, this is more an opinion based on indication data and on a study of the operation of the machines themselves than

a fact proved by true comparative data. It is also possible that the bowl classifier is better suited to the prevention of concentration of sulfides in the sand product.

In general application, it has been found that the bowl classifier not only lends itself to a wider range of adjustment than the single-stage classifier, but also has a wider range of flexibility in maintaining uniform conditions under a given set of adjustments. For this reason alone, it should be better suited to either maximum selective classification or the reverse.

Mr. Dyrenforth and Mr. McArthur cite data on operation at McIntyre-Porcupine as indication data in support of advantage to be gained by selective classification, this selective classification having been obtained by the addition of the bowl classifier operating between primary and secondary grinding circuits and in tandem closed circuit with single-stage classifiers in the secondary circuit. We do not know that equally good results might not have been obtained had single-stage classifiers of equal capacity to the bowl classifiers been used. The fact remains, however, that by the installation of bowl classifiers, relatively fine grinding on the sulfide particles was obtained and thereby a higher extraction made, even though the average over-all grind of the ore was considerably coarser.

More recent data on a similar operation is that of the West Springs mill in South Africa. An indication of the possible maximum selective action in the bowl classifier at this plant is shown in Table 34. Here again, however, there are no data to prove that an equal concentration of sulfides in the secondary circuit might not have been obtained with single-stage classifiers operating under the same conditions of circulating load, but we believe that the greater selectivity of the bowl classifier is indicated.

TABLE 34.—*Concentration of Pyrite*

| | Original Ore, Per Cent. | Primary Class. Sands, Per Cent. | Secondary (Bowl) Class. Sand, Per Cent. |
|---|---|---|---|
| Total $Fe_2S$ | 4.4–4.5 | 7.3–7.5 | 8.5–9.0 |
| $Fe_2S$ in −200 mesh | | 17.5 | 36 |

In Mr. Barker's summary, following the eight points of his stage-grinding discussion, he points out the relationship between ball size and particle size, mentioning inability to meet an ideal condition. He continues the comment with the mention that tonnage increase in going from single-stage to multiple-stage operation reflects a favorable power balance as a result of benefit derived in the shape of greater work done on such tonnage. Instead of the primary stage in such a case operating inefficiently when judged by single-stage standards, as suggested by Mr. Barker, is not the opposite more likely to be true, for if we accept Mr. Barker's third point that the greater the tonnage fed to a mill, the greater the tonnage of finished material produced, does it not naturally follow that the primary mill, because of the increased feed tonnage under conditions of stage grinding, will produce more tons of finished material even though the percentage of finished material from the primary circuit is less?

On the other hand, is it not natural to expect that the secondary mill, both because of reduced total tonnage and material more resistant to reduction, will produce less tonnage of finished material than when operating on the original feed under single-stage conditions?

As an illustration, let us assume two mills and two classifiers operating single stage in parallel, each mill receiving an original feed of 500 tons and receiving feed as classifier sand return amounting to 1000 tons, each mill thus receiving a total feed of 1500 tons. Assume that the 1000 tons return sand load from each classifier is the maximum

tonnage that the classifiers can handle. If these two grinding units were placed in two-stage grinding operation, the combined original feed tonnage of 1000 tons would be fed to one mill, operating in closed circuit with its classifier, the classifier still working up to maximum sand-raking capacity and returning 1000 tons, giving the mill a total feed tonnage of 2000 tons, whereas in the single-stage operation this mill received a total feed of only 1500 tons. Would not this mill, when receiving a total feed of 2000 tons, produce a greater tonnage of finished material than when receiving a total feed of only 1500 tons, even though the average particle size of the larger tonnage is greater than the average particle size on the smaller tonnage?

Now let us look at the secondary grinding unit. In this, since the classifier can rake only 1000 tons, the secondary mill can receive only 1000 tons of total feed, whereas before, when operated in the single-stage grinding set-up it received a total feed of 1500 tons. Not only is the mill unable to receive as great a tonnage as it did under conditions of single-stage grinding, but the 1000 tons of feed under the conditions of two-stage grinding is on the average more resistant to reduction than the total mill feed under the condition of single-stage grinding. The only advantage the secondary mill may have over the single-stage operation lies in the fact that the average particle size in mill feed is less under conditions of the secondary operation as compared to conditions under single-stage operation.

From the above, does it not seem possible that the increased tonnage of finished material produced in the primary circuit may be offset by the decreased tonnage produced in the secondary circuit, in which case, of course, the over-all grind would remain the same as under the condition of operating both grinding units as single-stage operation? Then, from this, may it not naturally follow that, if greater classifier capacity is provided for the secondary unit, so that the tonnage of feed to the secondary mill can be increased to as great or greater tonnage than that under the conditions of the single-stage grinding, full advantage may be taken of the increased efficiency of the primary circuit, plus any increase that may be obtained in the secondary circuit?

It may be well on some ores that an ideal operation should consist of maximum grinding accomplishment in the primary circuit, with the secondary circuit receiving a material largely ground past the separation mesh desired and containing sulfide of middling sizes on which the greater amount of selective classifying and grinding action is desired. As a rule we believe the particle size return from a secondary classifier to a secondary grinding mill, such as this operation would produce, is highly resistant to reduction, and the quantity reduced to the given mesh in this secondary mill will not compare favorably with the reduction in the primary mill. On the other hand, such reduction, even though it seems inefficient from the grinding standpoint, may be quickly reflected in the metallurgy, and if the power consumption per ton material finished is no greater for the primary and secondary circuits combined than when operating single-stage, some good has been accomplished.

Mr. Barker seems to tie the average size of feed particle directly to the ratio of circulating load. The average size of feed particle is not necessarily a function of circulating load, or, perhaps more clearly stated, while the ratio of circulation is a factor, the average size of feed particle may be either increased or decreased, regardless of increase, decrease or constant circulating ratio, depending on the closed-circuit hook-up, size of original feed, total tonnage of mill feed and probably several other conditions. From this it would then seem to follow that with two given flow sheets, differing only in number of classifiers and allocation to the different stages, the average size of feed particle is incidental to the more important factor of increased total mill-feed tonnage, permissible in that flow sheet having the greatest number of classifiers or classifiers with the greatest sand-raking capacity.

The justification for a tertiary circuit, and even perhaps in some cases for a secondary circuit, we believe should be examined from several standpoints. The range of reduction will come in for consideration, as will also the resistance to reduction in certain sizes by certain ores. In many cases, the mill layout will be given consideration, and necessarily so where tertiary grinding is under consideration. We believe that tertiary grinding will continue to receive the attention of investigators in their consideration of sulfide particle size and, perhaps, conditioning for maximum metallurgical results in the flotation circuit. Unfortunately the comprehensive work of Richards does not carry us down into the particle sizes normally dealt with today in flotation operations, but if the relative settling rates of gangue and sulfide particles as given by Richards for the larger sizes carries down through the smaller sizes some advantage should be gained in the selective classification of sulfide particles by working on the finer sizes found in the tertiary grinding circuit.

The flow sheet in Fig. 10 is suggested by a composite picture of the general trend as we see it. It is entirely possible that higher grinding efficiency and better metallurgical results might be obtained by combining classifiers, relocating classifiers and even combining stages of grinding. There is no doubt that all of the flow sheets from which this composite is made up were influenced largely by local conditions entirely outside of grinding efficiency and metallurgy, but from the data presented there does appear to be some grinding or metallurgical justification for the flow sheets that have been adopted.

# Elements of Operation of the Pneumatic Table

By Arthur F. Taggart* and R. L. Lechmere-Oertel,† New York, N. Y.

(New York Meeting, February, 1929)

This paper describes the result of a series of experiments run in the laboratory of the School of Mines, Columbia University, during the winter of 1927–28. It shows that the several operating adjustments of a pneumatic table produce effects in the action of a given coal that may be grouped into two classes, *viz.:* stroke length, speed and rocker-arm angle, which affect longitudinal travel; air supply and table slope (transverse and longitudinal), which determine transverse travel. The magnitude of the effect of the different adjustments varies. Some of the adjustments affect stratification of the bed, both as respects size and specific gravity of the bed components, as well as direction of travel.

Operation of a pneumatic table is fundamentally different from that of a wet table in that the former exerts, through the air supplied, a force on the particles upward away from the deck which is lacking on the wet table while, on the other hand, it lacks the positive control over cross travel that is supplied by the wash and feed water.

## Apparatus

The pneumatic table used is shown in Fig. 1. Deck *A* is 20 by 12 in. and consists of nainsook supported on slats that register with the riffles. Fig. 2 is a photomicrograph of the nainsook used. It shows that the cotton threads average about 0.13 mm. dia. and the apertures about 0.17 mm. The deck carries 12 riffles consisting of wooden strips, $\frac{3}{16}$ in. wide and $\frac{1}{4}$ in. high, laid parallel to the feed side of the table. The riffles terminate along a line starting on the feed side at a point 11 in. from the mechanism end and running to the corner formed by the coal side and slate end. Taper starts from a line that runs parallel to their terminal line through the junction of the upper riffle with the mechanism end. The height at the terminal line is about $\frac{1}{32}$ in. The deck with its supporting slats is carried on a framework consisting of rails *A*, sloping end rails *B*, and adjustable metal strips *C*, which latter permit variation in transverse slope. This frame is enclosed at the edges by means of heavy canvas, indicated in the sketch by wavy lines, which makes a flexible conduit between the deck and the stationary air chamber,

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and this in turn is connected with the air supply, as indicated. Within the upper end of chamber $D$ is a galvanized-iron plate, punched and bent roughly after the fashion of expanded-metal lath, the vanes turned so as to direct air diagonally toward the feed corner of the deck. The corner

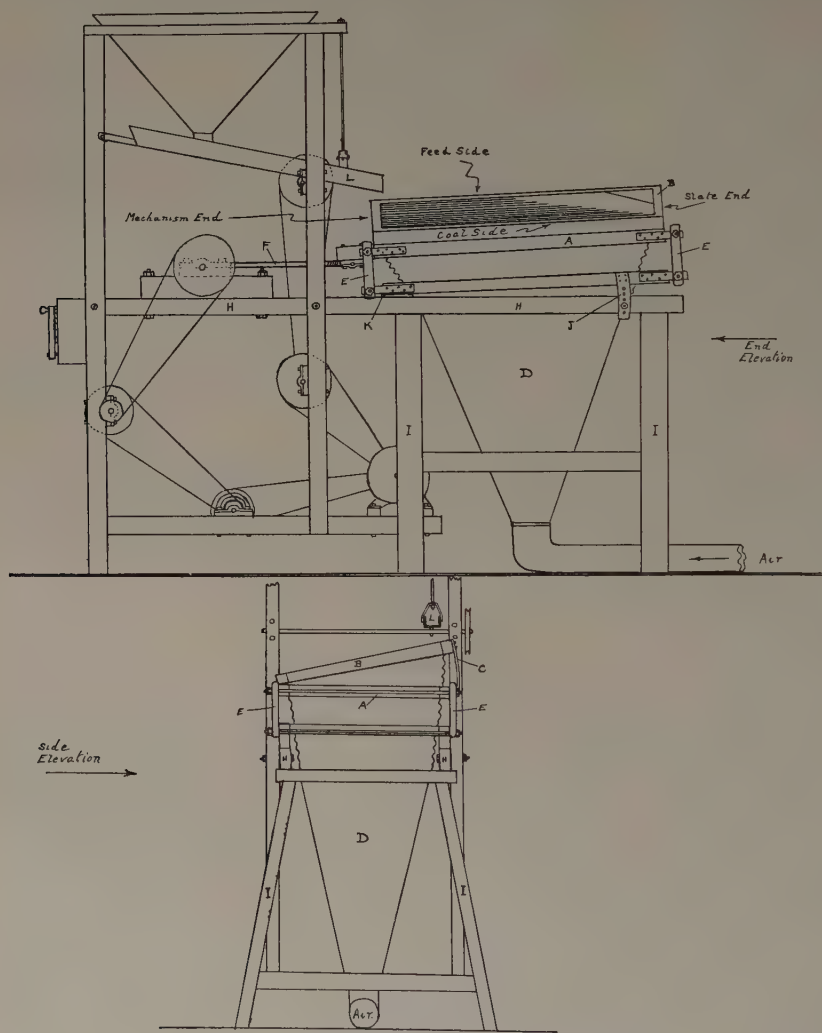


FIG. 1.—PNEUMATIC TABLE USED BY AUTHORS.

of the deck uncovered by riffles was covered during the runs by a right-triangular piece of cardboard 7 in. on a leg, which prevented excessive discharge of air at this part of the table, where, due to absence of bed, the resistance to passage of air was least. The deck framework is supported on four links or rocker arms $E$, inclined about $17\frac{1}{2}°$ from the

vertical, as shown, the exact inclination varying with the effective length of connecting rod *F*. The rocker arms are supported by the fixed framework *G*, *H*, *I*, etc. Longitudinal slope is varied by means of the arc supports *J* and pin support *K*. A simple variable-stroke eccentric actuates the deck through a system of cone pulleys to a ½-hp. motor. It was found unnecessary to accentuate reverse at the forward end of the stroke by means of a bumping block. A bumping-tray (Hooper) feeder *L*, is mounted on the same frame and driven from a second pulley on the motor shaft, so that it is possible to maintain constant feeder speed despite variations in table speed.

Air is supplied by means of a Clarage C. I. No. 7 blower run at constant speed, the volume supplied being controlled by the size of the inlet orifice. Air volume was measured by means of orifices of different sizes and water-gage pressure readings.

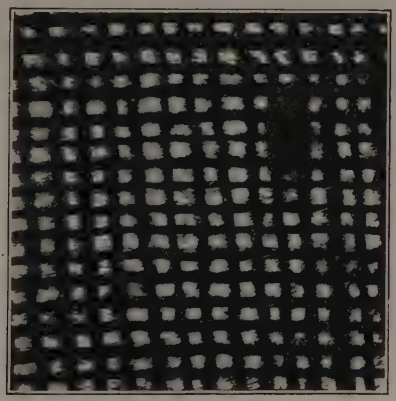

FIG. 2.—NAINSOOK COVER. × 10.

## TESTING PROCEDURE

The work was directed toward investigating, one at a time, the effects on performance of the table of air supply, speed, length of stroke, longitudinal slope, transverse slope and rocker-arm angle, all of the variables but the one immediately under investigation being held constant.

The material used was an artificial mixture of a relatively clean and not very soft bituminous coal, containing about 9 per cent. of bone and slate of +1.5 sp. gr. To this was added enough slate from a different coal to bring the total percentage of material +1.5 sp. gr. up to the figures indicated in the various tests, averaging about 15 per cent. This material was crushed and screened to pass a ¼-in. aperture Hum-mer screen and stay on a 1/10-in. aperture Hum-mer screen. It will be noted

in the sizing tests of products that a considerable amount of $-\frac{1}{16}$-in. material is recorded. The presence of these fines was due in part to imperfect screening of the feed, in part to degradation in handling.

Preliminary tests showed a feed rate of about 3.5 kg. per min. well suited to the size of table. Detailed figures of the actual feed rates are given in the records of the tests.

In each test the table was run until conditions became relatively constant; the entire discharge was then caught for a short interval in a cutter arranged to fit against the discharge edges of the table, and so compartmented as to deliver 8 products from $X_1$ to $X_8$, representing successively the discharges from 3-in. lengths along the discharge edge beginning at the mechanism end of the coal side.

The samples of table discharge were next separated into three groups, *viz.:* (*a*) specific gravity greater than 1.8; (*b*) specific gravity between 1.8 and 1.5; and (*c*) specific gravity less than 1.5; using solutions of zinc chloride. These fractions were then screened on round-hole punched-plate testing sieves of nominal apertures of $\frac{1}{8}$ and $\frac{1}{16}$ in. and the various products were weighed.

The table discharge was next arbitrarily divided, solely on a weight basis, into three classifications, namely, "coal," constituting the 70 per cent. of material discharged in the positions of lowest subscript value; "middling," the 20 per cent. of material discharged in the positions next to the coal; and finally "slate," the 10 per cent. of material discharged in the positions of highest subscript. The physical character of these three products when the table was operating to produce the best results was roughly as follows: coal was largely clean material of less than 1.5 sp. gr., slate was largely of +1.8 sp. gr., and middling was a mixture of clean coal (−1.5 sp. gr.), slate, and bone (1.5 to 1.8 sp. gr.).

Following this arbitrary classification, a "relative separation index" (R. S. I.) was calculated. This was done by first distributing the +1.5 sp. gr. material in the middling between "coal" and "slate" in the proportions in which such material was found in these classes in the original analyses and classification, then dividing the adjusted weight of +1.5 sp. gr. material in the adjusted "slate" by the weight of +1.5 sp. gr. material in the original feed. This R. S. I. is obviously the adjusted *actual recovery* of +1.5 sp. gr. material in the "slate," or the adjusted percentage rejection of waste, on the basis that the arbitrarily chosen 10 per cent. slate reject would correspond to an actual operation on the particular feed investigated. Such an assumption would be true only accidentally for any given feed. The alternative was to introduce another variable by having movable splitters, but since calculation automatically adjusts the position of discharge to maintain the weight classification set up, it is preferable.

A second measure of performance is obtained by determining the position on the discharge periphery of the table at which the center of mass of the total table discharge falls.

The way in which these two measures interpret the action of the table under various operating conditions is apparent from the discussions of the results of the tests, which follow.

## Effects of Variation in Quantity of Air Supplied

In this series of runs air volume was the variable and ranged from 172 to 520 cu. ft. per min., corresponding to 115 to 350 cu. ft. per min. per sq. ft. of table surface. (Note here, however, that on account of losses both in piping and at the flexible joint between the expander *D* (Fig. 1) and the table top, the figures for air per square foot of table top are not accurate, but they are an approximation to the truth and are substantially accurate relatively.) The other variables of operation were held constant at the following figures: speed, 320 strokes per min.; length of stroke, ½ in.; longitudinal slope, ⅝ in. per ft.; transverse slope, 3½ in. per ft.; rocker-arm angle, 17.5° from the vertical. The rate of feed was about 3200 g. per minute.

Tables 1 and 2 give the numerical results of the runs; Table 3 shows calculation of R. S. I., based on values read from Fig. 3.

Fig. 3 presents two independent sets of curves that interpret graphically the data of Table 1. The curves slanting upwardly to the right give at any point the percentage of the total weight of the feed that has discharged between that point on the discharge periphery and the mechanism end of the table. The other set of curves gives for any given rate of air supply at any given point on the discharge periphery the coal content of the material discharging at that point.

From an examination of the first set of curves it is apparent that for any point lengthwise of the table the average rate of flow down slope and the consequent solid discharge up to that point have increased with increase in volume of air supplied. From this fact it is to be concluded, as observation of the table in operation makes clear, that fluidity of the deck load increases with increase in air quantity. Observation indicated, and the indication was confirmed quantitatively, as will be seen later, that the quality of the operation improves with increased fluidity of the bed up to a point where the amount of air becomes excessive. Then blow holes appear in the bed and the finer particles are lifted some distance above the surface. (See Fig. 55*b*.) With such an excess of air the quality of the work falls off rapidly and continuously.

It is worthy of note that a straight line on this set of axes would represent uniform discharge along the full length of the coal side of the table. The inflection that occurs at about the 16-in. point is due to two facts: (1) At about this point the bed thins out so much that the lifting

TABLE 1.—*Specific-gravity Analyses of Table Discharges with Different Rates of Air Supply*

$F$ represents all material under 1.5 sp. gr.: *i. e.*, coal.
$S_1$ represents all material between 1.5 and 1.8 sp. gr.: *i. e.*, bone.
$S_2$ represents all material over 1.8 sp. gr.: *i. e.*, slate.
$X_{1,etc.}$ represent positions along coal side. See page 158.

| Diameter of orifice, in. | 2 | 2½ | 3 | 3½ | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| Water gage, in. | 10.0 | 8.5 | 6.9 | 5.0 | 3.7 | 1.75 | 1.1 |
| Air, cu. ft. per min. | 172 | 250 | 322 | 375 | 420 | 455 | 520 |
| Weight of sample, g. | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| Calculated per cent. of feed +1.5 sp. gr. | 19.30 | 12.66 | 14.06 | 12.60 | 12.19 | 19.48 | 16.57 |
| Position of center of mass of discharge in inches from feed end | 13.75 | 12.20 | 10.55 | 9.00 | 8.66 | 7.50 | 6.72 |

| Sample Mark | Sp. Gr. Classification | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages | Total Weight of Sample, G. | Partial Weights, G. | Percentages |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_1$ | $F$ | 0.7 | 0.7 | 100.0 | 13.9 | 13.9 | 100.0 | 87.2 | 84.5 | 97.0 | 172.2 | 166.9 | 96.9 | 187.6 | 183.2 | 97.7 | 285.2 | 274.9 | 96.5 | 307.3 | 294.4 | 96.0 |
| | $S_1$ | | | | | | | | 2.7 | | | 1.6 | | | 1.9 | | | 2.7 | | | 4.9 | |
| | $S_2$ | | | | | | | | | | | 3.7 | | | 2.5 | | | 7.6 | | | 8.0 | |
| $X_2$ | $F$ | 4.2 | 4.15 | 99.0 | 57.3 | 55.6 | 97.0 | 95.5 | 92.6 | 97.0 | 133.4 | 128.7 | 96.4 | 147.5 | 143.1 | 97.1 | 162.5 | 156.0 | 96.0 | 187.8 | 174.7 | 93.0 |
| | $S_1$ | | 0.05 | | | 1.7 | | | 2.9 | | | 4.7 | | | 4.4 | | | 6.5 | | | 13.1 | |
| | $S_2$ | | | | | | | | | | | | | | | | | | | | | |
| $X_3$ | $F$ | 73.4 | 68.8 | 93.7 | 150.0 | 141.7 | 94.5 | 157.5 | 152.8 | 97.0 | 167.0 | 160.7 | 96.2 | 166.0 | 159.5 | 96.1 | 148.3 | 139.9 | 94.3 | 169.3 | 151.9 | 89.7 |
| | $S_1$ | | 4.1 | | | 3.3 | | | 3.3 | | | 3.5 | | | 4.0 | | | 2.7 | | | 9.5 | |
| | $S_2$ | | 0.5 | | | 5.0 | | | 1.4 | | | 2.8 | | | 2.5 | | | 5.7 | | | 7.9 | |
| $X_4$ | $F$ | 216.7 | 188.6 | 87.0 | 234.4 | 215.6 | 91.8 | 236.7 | 227.3 | 96.0 | 208.8 | 198.4 | 95.1 | 199.3 | 184.4 | 92.5 | 159.4 | 133.9 | 84.0 | 167.1 | 135.4 | 81.0 |
| | $S_1$ | | 28.1 | | | 18.8 | | | 9.4 | | | 10.4 | | | 14.9 | | | 25.5 | | | 31.7 | |
| | $S_2$ | | | | | | | | | | | | | | | | | | | | | |
| $X_5$ | $F$ | 332.3 | 268.3 | 80.7 | 286.3 | 251.2 | 87.7 | 250.7 | 221.0 | 88.2 | 207.6 | 179.5 | 86.5 | 200.4 | 164.9 | 82.3 | 166.8 | 93.3 | 56.0 | 133.3 | 74.4 | 55.7 |
| | $S_1$ | | 14.5 | | | 4.8 | | | 14.2 | | | 5.2 | | | 15.6 | | | 12.1 | | | 15.1 | |
| | $S_2$ | | 49.5 | | | 30.3 | | | 15.5 | | | 22.9 | | | 19.9 | | | 61.4 | | | 43.8 | |
| $X_6$ | $F$ | 271.0 | 214.0 | 79.0 | 181.5 | 147.9 | 81.5 | 133.3 | 74.3 | 55.7 | 89.7 | 37.9 | 42.3 | 84.4 | 41.3 | 49.0 | 65.2 | 7.0 | 10.7 | 32.0 | 3.4 | 10.6 |
| | $S_1$ | | 3.8 | | | 2.8 | | | 10.6 | | | 3.1 | | | 6.3 | | | 0.8 | | | 0.3 | |
| | $S_2$ | | 53.2 | | | 30.8 | | | 48.4 | | | 48.7 | | | 36.8 | | | 57.4 | | | 28.3 | |
| $X_7$ | $F$ | 77.7 | 54.7 | 70.5 | 76.6 | 47.5 | 62.1 | 39.1 | 6.9 | 17.6 | 21.3 | 1.9 | 8.9 | 14.8 | 1.7 | 11.5 | 12.6 | 0.2 | 1.6 | 3.2 | 0.1 | 3.1 |
| | $S_1$ | | 1.7 | | | 2.2 | | | 2.5 | | | 0.4 | | | 0.2 | | | 12.4 | | | | |
| | $S_2$ | | 21.3 | | | 26.9 | | | 29.7 | | | 19.0 | | | 12.9 | | | | | | 3.1 | |
| $X_8$ | $F$ | 24.0 | 7.7 | 32.1 | ←——Discharge over end of table | | | | | | | | | | | | | | | | | |
| | $S_1$ | | 0.8 | | | | | | | | | | | | | | | | | | | |
| | $S_2$ | | 15.5 | | | | | | | | | | | | | | | | | | | |

TABLE 2.—*Sizing Analyses of Table Discharges with Different Rates of Air Supply*

[For Explanation of Letters, see Table 1]

| Air, Cu. Ft. per Min... | | 172 | | | 250 | | | 322 | | | 375 | | | 420 | | | 455 | | | 520 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | |
| Size Group | | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ | −¼″ + ⅛″ | −⅛″ + 1/16″ | −1/16″ |
| $X_1$ | $F$ | | | 0.7 | 10.1 | 1.2 | 2.6 | 11.3 | 52.3 | 20.9 | 38.6 | 105.2 | 23.1 | 57.5 | 103.2 | 22.5 | 58.9 | 182.1 | 33.9 | 89.8 | 179.3 | 25.3 |
| | $S_1$ | | | | | | | 0.3 | 0.1 | | 0.3 | 1.1 | 0.2 | 1.1 | 0.5 | 0.3 | 1.1 | 1.2 | 0.4 | 2.8 | 1.4 | 0.7 |
| | $S_2$ | | | | | | | 0.1 | 0.3 | 1.9 | 0.4 | 1.9 | 1.4 | 0.3 | 0.8 | 1.4 | 1.3 | 2.8 | 3.5 | 0.9 | 4.5 | 2.6 |
| $X_2$ | $F$ | 3.95 | 0.1 | 0.1 | 43.0 | 10.0 | 2.6 | 32.6 | 48.0 | 12.0 | 49.5 | 69.2 | 10.0 | 69.1 | 62.0 | 12.0 | 61.0 | 88.0 | 7.0 | 86.7 | 83.0 | 5.0 |
| | $S_1$ | | | | 0.5 | | * | 1.3 | | * | 0.7 | | * | 2.0 | | * | 1.2 | | * | 4.7 | | * |
| | $S_2$ | 0.05 | | | 1.0 | | | 0.2 | 0.4 | | 0.5 | 1.3 | | 0.5 | 1.0 | | 1.2 | 3.0 | | 2.0 | 4.0 | |
| $X_3$ | $F$ | 61.9 | 5.4 | 1.5 | 105.5 | 32.3 | 3.9 | 64.4 | 81.3 | 7.1 | 80.5 | 74.2 | 6.0 | 96.6 | 60.2 | 2.7 | 92.5 | 45.7 | 1.7 | 103.7 | 46.3 | 1.9 |
| | $S_1$ | 4.0 | 0.1 | | 2.8 | 0.4 | 0.1 | 2.5 | 0.7 | 0.1 | 1.9 | 1.0 | 0.6 | 3.1 | 0.6 | 0.3 | 1.7 | 0.7 | 0.3 | 7.8 | 1.5 | 0.2 |
| | $S_2$ | 0.5 | | | 4.8 | 0.1 | 0.1 | 0.4 | 0.5 | 0.5 | 0.8 | 1.0 | 1.0 | 0.6 | 1.4 | 0.5 | .9 | 3.9 | 0.9 | 3.3 | 3.9 | 0.7 |
| $X_4$ | $F$ | 113.0 | 62.0 | 13.6 | 149.0 | 62.0 | 4.6 | 101.0 | 120.8 | 5.5 | 115.0 | 80.0 | 3.4 | 131.0 | 52.0 | 1.4 | 105.9 | 27.0 | 1.0 | 107.4 | 27.0 | 1.0 |
| | $S_1$ | 12.0 | | * | 3.8 | | * | 3.7 | | * | 3.5 | | * | 8.0 | | * | 3.5 | | * | 14.0 | | * |
| | $S_2$ | 12.0 | 2.0 | | 12.6 | 0.6 | | 1.8 | 1.8 | | 4.0 | 2.5 | | 1.8 | 3.0 | | 11.5 | 7.5 | | 11.5 | 6.5 | |
| $X_5$ | $F$ | 109.7 | 143.8 | 14.8 | 150.1 | 96.7 | 4.4 | 102.6 | 115.1 | 3.3 | 106.5 | 70.7 | 2.3 | 130.2 | 34.0 | 0.7 | 74.3 | 18.4 | 0.6 | 61.7 | 12.1 | 0.6 |
| | $S_1$ | 10.7 | 3.4 | 0.4 | 3.3 | 1.1 | 0.4 | 11.5 | 2.5 | 0.2 | 3.9 | 1.0 | 0.3 | 13.9 | 1.4 | 0.3 | 10.4 | 1.5 | 0.2 | 14.7 | 0.3 | 0.1 |
| | $S_2$ | 40.3 | 8.4 | 0.8 | 26.9 | 2.8 | 0.6 | 8.1 | 5.6 | 1.8 | 12.5 | 8.4 | 2.0 | 12.9 | 5.7 | 1.3 | 43.2 | 16.0 | 2.2 | 33.7 | 9.3 | 0.8 |
| $X_6$ | $F$ | 69.2 | 131.5 | 13.3 | 83.2 | 63.3 | 1.4 | 34.2 | 38.4 | 1.7 | 25.4 | 11.9 | 0.6 | 34.5 | 6.5 | 0.3 | 4.3 | 2.4 | 0.3 | 1.7 | 1.6 | 0.1 |
| | $S_1$ | 1.5 | 2.1 | 0.2 | 1.0 | 1.5 | 0.3 | 8.6 | 1.5 | 0.5 | 2.1 | 0.8 | 0.2 | 6.0 | 0.3 | | 0.5 | 0.1 | 0.2 | 0.3 | | |
| | $S_2$ | 33.6 | 17.9 | 1.7 | 23.0 | 6.6 | 1.2 | 29.7 | 16.2 | 2.5 | 33.4 | 13.7 | 1.6 | 29.6 | 6.5 | 0.7 | 43.4 | 13.1 | 0.9 | 22.7 | 5.1 | 0.5 |
| $X_7$ | $F$ | 13.5 | 37.9 | 3.3 | 18.4 | 28.3 | 0.8 | 2.4 | 4.3 | 0.2 | 0.9 | 0.9 | 0.1 | 1.2 | 0.4 | 0.1 | | 0.2 | | | 0.1 | |
| | $S_1$ | 0.5 | 1.1 | 0.1 | 1.3 | 0.9 | | 1.5 | 0.9 | 0.1 | 0.3 | 0.1 | | 0.2 | | | | | | | | |
| | $S_2$ | 6.3 | 12.7 | 2.3 | 9.1 | 14.8 | 3.0 | 13.0 | 15.0 | 1.7 | 12.5 | 5.8 | 0.7 | 9.9 | 2.8 | 0.2 | 9.6 | 2.4 | 0.4 | 2.4 | 0.7 | |
| $X_8$ | $F$ | 0.2 | 6.3 | 1.2 | ←—Discharge over end of table | | | | | | | | | | | | | | | | | |
| | $S_1$ | 0.1 | 0.6 | 0.1 | | | | | | | | | | | | | | | | | | |
| | $S_2$ | 0.9 | 10.8 | 3.8 | | | | | | | | | | | | | | | | | | |

* These figures are calculated from the graphs.

effect of the air is dissipated through it, the action being on individual particles rather than on a mass, and consequently the characteristic fluidity is greatly diminished or lost entirely and individual particles must climb over the riffles with but little help from the air and none

TABLE 3.—*Calculations for R. S. I.; Air Supply the Variable*

| Air, Cu. Ft. per Min. | 172 | 250 | 322 | 375 | 420 | 455 | 520 |
|---|---|---|---|---|---|---|---|
| Total impurity* in sample of 1000 g. | 193.0 | 126.6 | 140.6 | 126.0 | 121.9 | 194.8 | 165.7 |
| Impurity in coal, g. | 111.9 | 58.0 | 29.8 | 28.0 | 30.2 | 38.2 | 48.6 |
| Impurity in middling, g. | 44.5 | 33.1 | 44.3 | 31.8 | 35.2 | 71.7 | 50.6 |
| Impurity in slate, g. | 36.6 | 35.5 | 66.5 | 66.2 | 56.5 | 84.9 | 66.5 |
| Middling impurity allotted to coal, g. | 33.5 | 20.5 | 13.7 | 8.9 | 12.3 | 22.2 | 21.4 |
| Middling impurity allotted to slate, g. | 11.0 | 12.6 | 30.6 | 22.9 | 22.9 | 49.5 | 29.2 |
| Adjusted impurity in coal, g. | 145.4 | 78.5 | 43.5 | 36.9 | 42.5 | 60.4 | 70.0 |
| Adjusted impurity in slate, g. | 47.6 | 48.1 | 97.1 | 89.1 | 79.4 | 134.4 | 95.7 |
| R. S. I. | 24.6 | 38.0 | 69.0 | 70.7 | 65.2 | 69.0 | 57.7 |

* Material + 1.5 sp. gr.

from their neighbors. (2) Inspection of the curves indicates that their point of meeting, had these two conditions not interfered, would have been at about abscissa 18. For such a set of curves, the one for 375

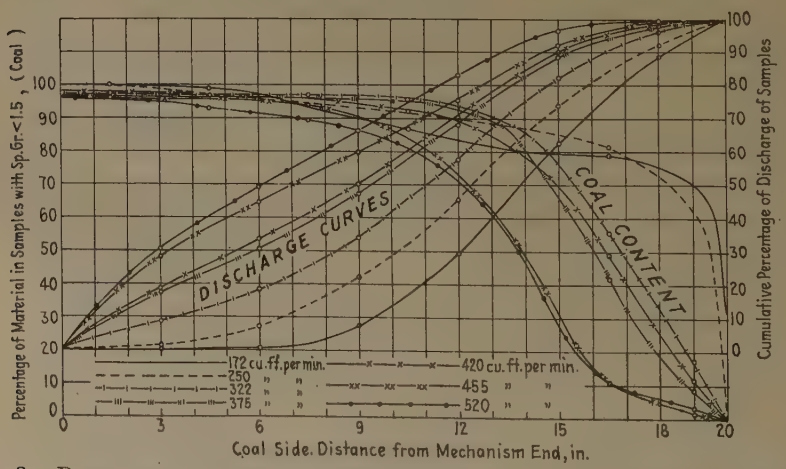


FIG. 3.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERENT QUANTITIES OF AIR.

cu. ft. of air per min. would approach nearest the straight line. This rate, later analysis showed, is the one producing optimum separation, from which it seems that a uniform discharge rate along the coal side is a condition to be sought. Owing to the difficulty of obtaining a

perfectly uniform taper on a riffle down to zero height, it happened that the last 1½ in. of the lowest riffle was maintained at its minimum height of rather over 1/32 in. Coupled with this it was found, experimentally, that the great majority of slate particles discharging towards that end of the deck had a thickness of under 1/12 in., which would bring the height of the center of gravity of most of them at or below the riffle height. This fact taken in conjunction with the former would make discharge of these particles difficult before the end of the riffle was reached, and this in turn, would result in the continuation of the discharge curves as noted.

The other set of curves on Fig. 3 shows that with the exception of the two lowest and the highest air quantities the extent of cleaning indicated was much the same for the first 6 or 7 in., say one-third the length of the table. Thereafter distinct differences became apparent in the character of the discharge at any given point along the coal side for different air quantities. When the slate-coal corner was approached the quality of the discharge under different air conditions was such as to permit grouping of these discharges into three classes, *viz.:* those of highest coal content, represented by the curves for the two smallest air-supply rates; those of lowest coal content, indicated by those curves representing the two highest rates of air supply; and an intermediate group representing the three intermediate rates. This divergence of the curves toward the right of the chart indicates: (*a*) At the two lowest air rates no substantial separation of coal and slate was begun until within 3 or 4 in. of the slate end. (*b*) At the highest air rates, by the time the material had reached a point three-quarters of the distance toward the slate end, substantially all of the coal had been separated and, as is shown by the "discharge curves," around 90 per cent. of the material had been discharged by this time. For the remaining length of the table, therefore, the deck was acting principally as a transporting means for refuse. (*c*) The middle group of three curves represents an operation in which, at about the three-quarter point, the product remaining to be treated carried about 30 to 40 per cent. of worthless material and amounted to about 20 per cent. of the original weight; the rate of elimination of waste from that point on was practically a straight line function, and, therefore, within this range of air quantities, this corner of the table was properly loaded. (For discussion of an ideal coal-content curve see page 175.) These coal-content curves, therefore, indicate that, with the least air quantities, the table separation was deferred until the material had almost reached the slate end, the table being distinctly overloaded at this end and being, on these accounts, incapable of doing any effective separation; with the highest air quantities the deck was distinctly underloaded near the slate end and consequently overloaded near the mechanism end; while with the intermediate quantities the loading was substantially correct.

Fig. 4 shows the weights of clean coal, bone and slate of the different sizes in samples taken at various points along the coal side of the table, plotted against the distance in inches from the mechanism end at which the respective samples were caught. Study of the curves shows: (1) That not only was the peak of the discharge rate for coarse coal reached before that for intermediate coal, and the peak for coarse slate before that for intermediate slate, but also that the peaks for both the coarse coal and slate were reached before the peak for either intermediate coal or slate had been attained; (2) that the peaks of the discharge rates for coarse coal and coarse slate are about 2¼ in. apart along the table length, and for intermediate coal and intermediate slate about 1½ in. apart. Cleanliness of separation increases with increase in this spread, and if the peaks are too close together, as in Fig. 4, where intermediate

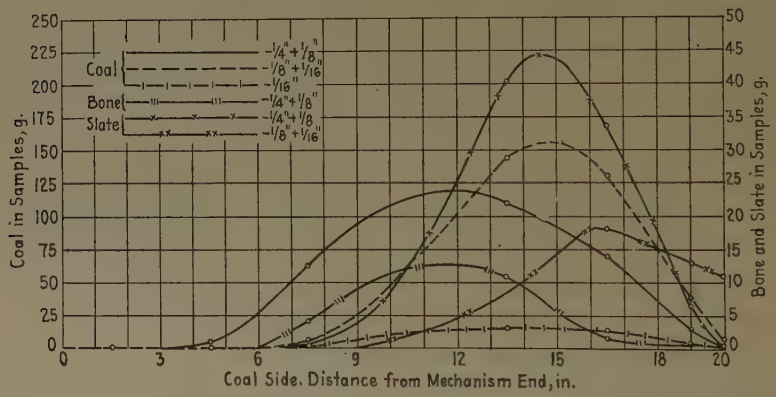


FIG. 4.—POSITION OF DISCHARGE WITH AIR EQUAL TO 172 CU. FT. PER MINUTE.

coal and coarse slate are discharging over almost identically the same range, and coarse slate is at half its maximum rate where coarse coal is at its maximum, separation is almost entirely lacking.

The physical interpretations of the points noted in connection with Fig. 4 are as follows: (1) Since rate of flow down slope is a function of the liquidity of the flowing mass, all other things remaining constant, it appears that in this test the liquidity was slight, since the beginning of discharge was deferred until the bed had traveled nearly 6 in. at right angles to the slope, and the main part of the bed did not discharge until after 12 to 15 in. of such longitudinal travel. When this behavior is compared with that of water on a slope of 3½ in. per ft., the extreme lack of fluidity may be appreciated. (2) The material that first leaves the coal side of the deck is that which is on top of the bed. Since the riffles get lower gradually toward the slate end, successively lower strata of the bed are left unsupported laterally by the lowest riffle and so are successively discharged. Thus the positions of discharge of the classes of

material, as portrayed in Fig. 4, indicate generally the nature of the stratification of the bed. (3) Fig. 4 shows that stratification in this run was of the same type as that effected when a mass of particles of different sizes is shaken in a box or pan. Under such circumstances the fine particles work down through the interstices of the mass to the bottom, leaving the upper layers distinctly coarser than the lower. It appears, therefore, that the velocity of the air rising through the bed was so low that its suspending effect on the solid particles was not effectively greater than the air substantially at rest in a box, for example.

It is not to be inferred from the preceding discussion that the riffles have anything to do with stratification or with the order in which different classes of material are discharged from the deck. They merely serve to slow down transverse travel and thereby increase longitudinally the distance over which discharge takes place.

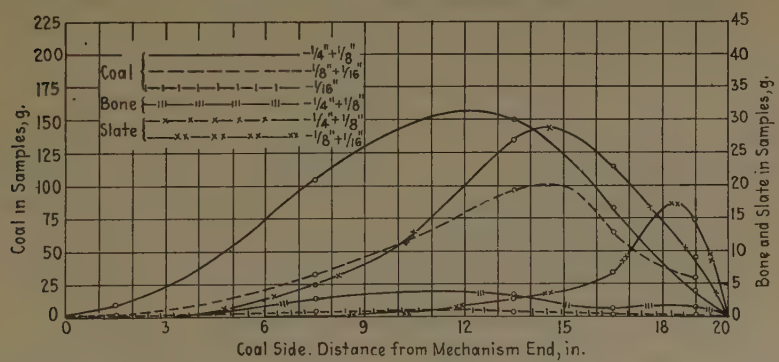


FIG. 5.—POSITION OF DISCHARGE WITH AIR EQUAL TO 250 CU. FT. PER MINUTE.

Some stratification according to specific gravity occurred in this run, as is indicated by the fact that the point of beginning of discharge of coarse slate is to the right of that for coarse coal; likewise the point of beginning of discharge of intermediate coal falls on the mechanism side of the point at which intermediate slate begins to come over.

In Fig. 5 the same data are portrayed graphically for 250 cu. ft. of air per min. Note that the point of commencement of discharge for all products has been moved toward the mechanism end; that the peaks for coarse and intermediate coal and coarse slate have been only slightly moved as compared to the preceding run, but that the peak for intermediate slate has been moved distinctly to the right; that the spread between the peaks of coarse coal and coarse slate has, if anything, closed up slightly, while the distance between the peaks for intermediate coal and intermediate slate has been increased; finally that the degree of stratification indicated differs but little from that in the first run.

The physical interpretation of the relative positions of the curves on Fig. 5 and their comparative positions with respect to those on Fig. 4 is as follows: (1) Increase in quantity of air has increased the liquidity of the bed and thereby permitted more rapid flow down slope, as is evidenced by the earlier beginning of discharge of all products. (2) The character of the stratification is essentially similar with 250 cu. ft. of air

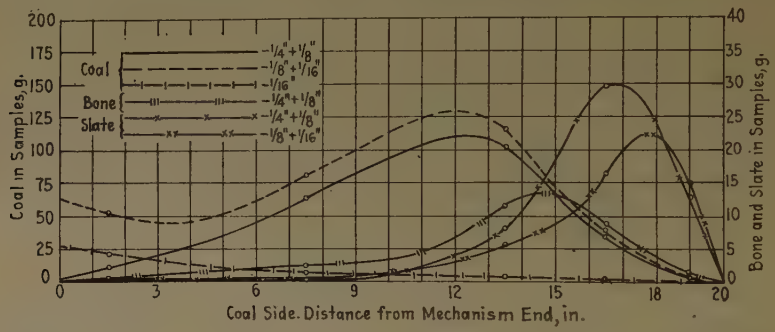


FIG. 6.—POSITION OF DISCHARGE WITH AIR EQUAL TO 322 CU. FT. PER MINUTE.

per min. to that with 172 cu. ft. (3) The fluidity of the mass of the bed is as yet insufficient to permit marked stratification of large particles of the same size and different specific gravities, but the curves show that intermediate slate has segregated more completely from coarse than in the previous experiment, although the coal is not similarly affected.

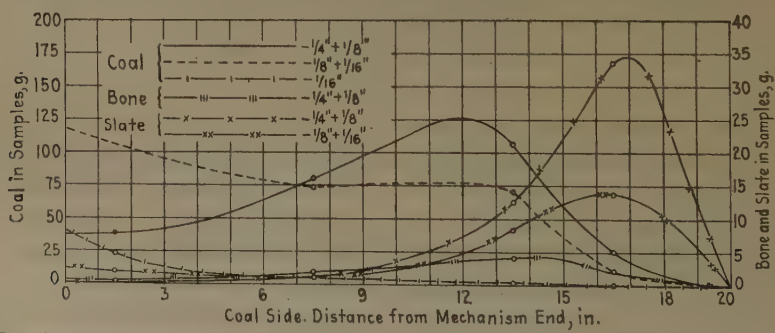


FIG. 7.—POSITION OF DISCHARGE WITH AIR EQUAL TO 375 CU. FT. PER MINUTE.

Fig. 6 is markedly different from Fig. 5 and shows the beginning of effective work by the table. The positions of the different sizes of coal have reversed, although this reversal has not extended to the slate. The peaks of the coal and slate discharge curves, for both coarse and intermediate sizes, have been spread to 4.5 or 5 in. apart as against 2.5 to 3.5 in. in the preceding run. The peak of the bone discharge has been moved from a point substantially coinciding with that of the coarse slate

to a point about halfway between the coal and slate peaks, which is about where it belongs.

Fig. 7 indicates the optimum conditions for this series of runs. Both fine and intermediate coal started discharging before coarse coal; for both fine and intermediate the discharge was substantially at a decreasing rate, while the coarse was correspondingly held back.

This situation is seen more clearly in the upper set of curves in Fig. 8, in which the ordinates are expressed in percentages of the total amount of each class of material present in the feed. Here the order in which discharge starts is indicated as fine coal, intermediate coal, coarse coal, fine slate, bone (coarse bone only, fine not included),

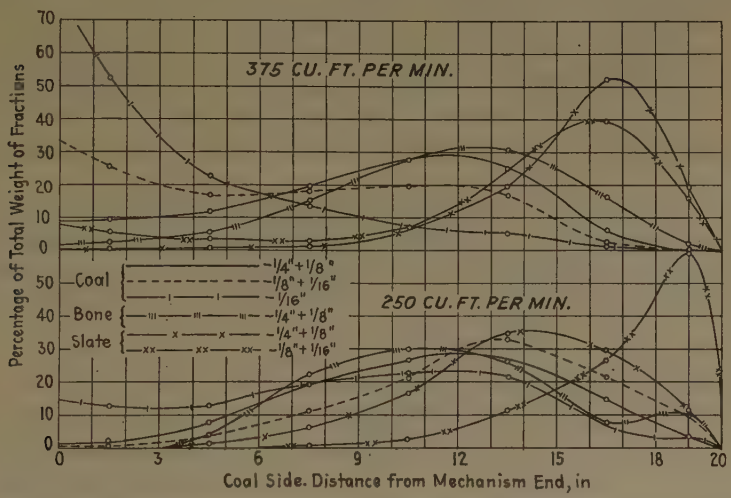


FIG. 8.—CHANGE IN RELATIVE POSITIONS OF SIZE AND SPECIFIC-GRAVITY FRACTIONS OF DISCHARGE WITH VARIATION OF AIR SUPPLY.

coarse slate, and this same order is maintained when the positions of maximum discharge rate are considered. Comparison of these curves with the 250-ft.-per-min. curves plotted at the bottom of Fig. 8, brings out clearly the reversal that has occurred.

The separation of the peaks of the coarse slate and coarse coal discharge curves is 5 in. Intermediate coal discharged at its maximum rate at the mechanism end of the coal side, 16.5 in. from the peak for intermediate slate, and, as will be developed in considering Fig. 12, the spacing between the centers of mass of these two discharges was near the maximum for the series of runs. The peak of the bone curve falls in the valley between the other two sets.

These curves make apparent the full and proper effect of the air, which is to offer such resistance to fall of the solid particles, thrown away from the supporting surface by the motion of the deck, that these

particles may fall at different rates according to the laws that govern the movement of discrete particles in a resisting fluid. Under these laws the rates of fall increase with increase in specific gravity and size, *i. e.*, with increase in effective weight. The order of decreasing falling velocities for the particles present on the table deck is coarse slate, fine slate

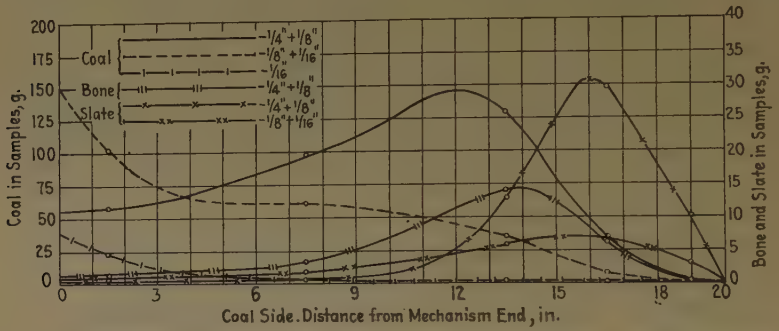


FIG. 9.—POSITION OF DISCHARGE WITH AIR EQUAL TO 420 CU. FT. PER MINUTE.

and bone, coarse coal, intermediate coal, fine coal, and this is precisely the order of stratification, as pointed out in the preceding paragraph.

The curves in Fig. 9 indicate no substantial differences between this test and the preceding one. The order of commencement of discharge

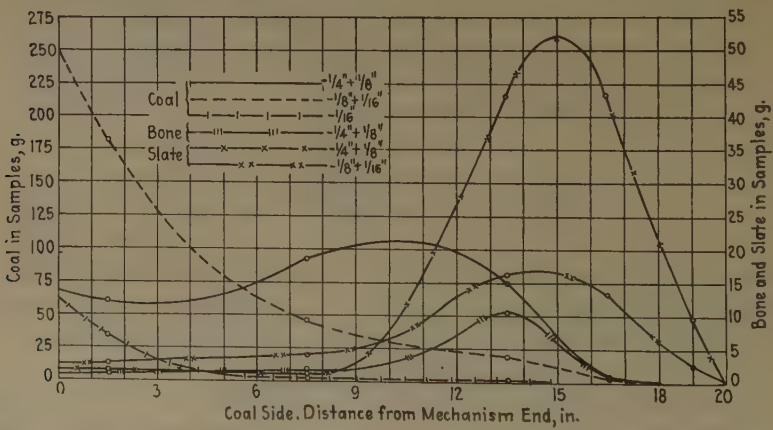


FIG. 10.—POSITION OF DISCHARGE WITH AIR EQUAL TO 455 CU. FT. PER MINUTE.

and the positions of the peaks are practically coincident in the two runs, and what has been said about Fig. 7 applies to Fig. 9.

The curves in Fig. 10 show an operation of the same general character as those portrayed in Figs. 7 and 9, with, however, two characteristic differences. In the first place, the whole discharge has been moved back toward the mechanism end of the table, and, as a result, there has been some crowding together of the positions of the discharge peaks

for the coarse sizes of slate and coal. This is disadvantageous. In the second place, the peaks of the slate discharge curves have been distinctly accented, which means that the bulk of the slate has been moved well

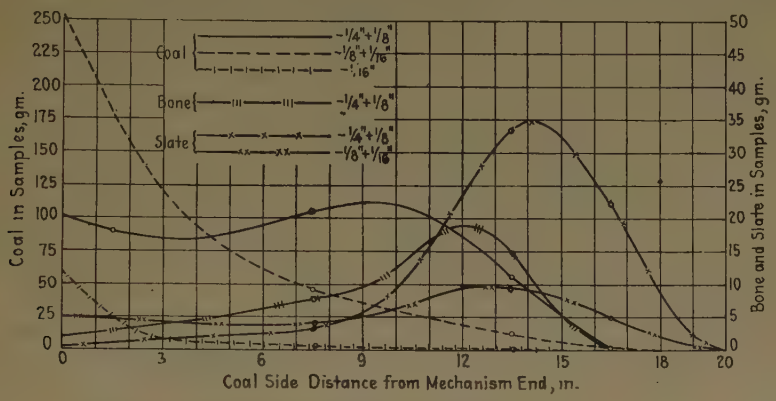


FIG. 11.—POSITION OF DISCHARGE WITH AIR EQUAL TO 520 CU. FT. PER MINUTE.

along toward the slate end before discharging. Unfortunately, however, the bulk of the bone and a considerable part of the coarse coal have been moved forward with the slate so that the grade of the reject has been

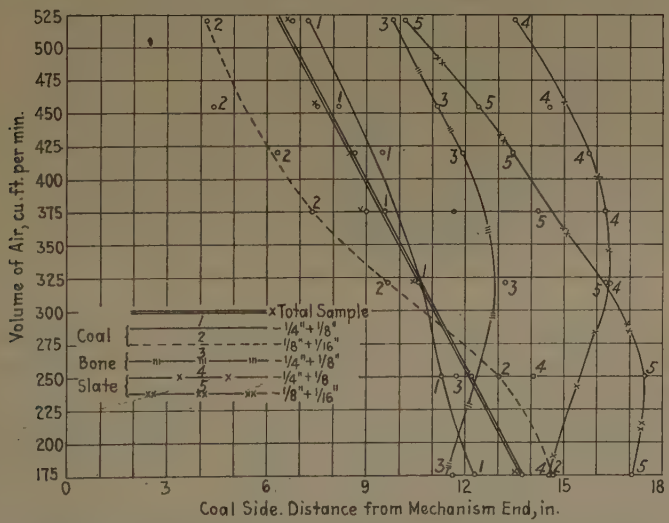


FIG. 12.—RELATION BETWEEN POSITIONS OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND QUANTITY OF AIR SUPPLY.

distinctly raised, with corresponding detriment to the economy of the operation.

Fig. 11 shows further movement in the direction indicated in discussing Fig. 10.

Fig. 12 is a summary of the preceding five figures in that it presents the variation in position along the coal side of the centers of mass of the discharge of the different sizes of the three specific-gravity classes or grades investigated, and also the variation in position of discharge of the center of mass of the entire bed. The curve showing the shift in position of the whole bed indicates substantially straight-line variation of this function with change in air supply. In other words, since all other conditions were held constant, it appears that the liquidity of the bed is a direct function of the quantity of air passed through it.

The curve for coarse coal roughly approximates that of the whole mass, and the curve for intermediate coal shows no marked variation therefrom. On the other hand, the curves for coarse slate and bone show that as the air supply increased up to 320 cu. ft. per min. there was a movement of the position of the discharge of the center of mass of these products toward the slate end, while with greater volumes of air

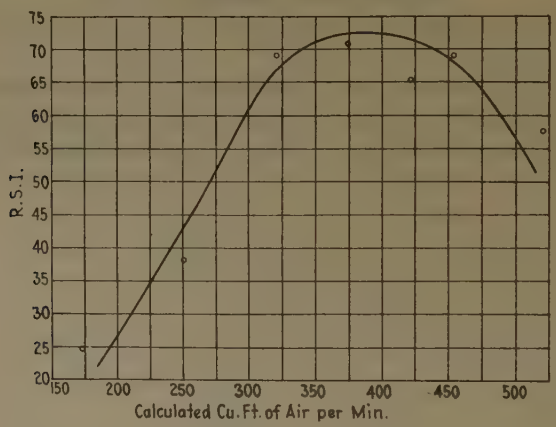


Fig. 13.—R. S. I.—air.

the point of discharge shifted back again toward the mechanism end. A similar tendency is shown by the curve for intermediate slate, but the point of reversal comes early in the series of tests. Separation of coal from slate will occur with maximum ease when the mean positions of discharge of the centers of mass of the two products are furthest separated along the discharge edge of the table. This maximum separation occurs in these curves somewhere between the abscissas 350 and 400, so that the optimum condition as indicated by this method of analysis accords with that reached by the two preceding methods.

Fig. 13 shows the relation between the relative separating index and air quantity and, by a fourth method of analysis, indicates the optimum air quantity at somewhere between 350 and 400 cu. ft. of air per minute.

## General Conclusions as to Air Supply

The ideal quantity of air is that which, rising through the bed, offers sufficient resistance to the fall of particles to bring about stratification on the basis of both specific gravity and size. Under such conditions the bed flows readily. The shaking motion must be sufficiently pronounced so that it, in conjunction with the rising current of air, repeatedly throws the mass into partial suspension, and thus permits relative motion among the particles according to the forces acting upon them. Under such circumstances the coarse slate settles to the table surface, and the coarse coal forms a layer on top of it, both settling according to the well recognized laws governing the settlement of solids in fluids. The fines, both coal and slate, tend to settle through the interstices of these coarse particles after the latter have come to rest. The rising current of air should be sufficient to prevent such settlement in the case of the coal, but the fine slate should, of course, settle below the coarse coal. Thereafter successive layers are sheared off by gravity as their support is removed along the coal side by reason of the tapering riffles, and the order of discharge should be fine coal, coarse coal, bone and slate. Fig. 4 shows a condition in which the air quantity is insufficient to offer effective resistance to the settlement of the fine slate and consequently this material is the lowest in the bed. Fig. 7 shows the peak of the intermediate-slate discharge substantially under the peak of the coarse-slate discharge, but Fig. 12 shows that at this air quantity, *viz.*, 375 cu. ft. per min., the position of the center of mass of the discharge of intermediate slate has moved definitely to the left of that of the coarse slate. These two figures, then, considered together, bearing in mind that 375 cu. ft. per min. was the experimental point of maximum efficiency, indicate that coarse and intermediate slate mixed together, the latter, however, slightly the higher, is the most desirable condition as regards stratification of the slate.

## Effects of Variation in Length of Stroke

The results of tests run with an air supply of 322 cu. ft. per min.; transverse slope, 3½ in. per ft.; longitudinal slope, ⅝ in. per ft.; rocker-arm angle, 17½°; and 320 strokes per min., are given in Tables 4 and 5, and the calculations for R. S. I. in Table 6. The rate of feed was about 4000 g. per min. Fig. 14 shows that with ¼-in. stroke 90 per cent. of the material came off in the first 9 in. along the coal side of the table, and with ⅜-in. stroke 90 per cent. had discharged in less than 11 in. At the other extreme, with ¾-in. stroke, material was moved along the table so rapidly that but 33 per cent. discharged within the first 9 in. The bed, as might be inferred, was distinctly sluggish with the shorter strokes, and material piled up rather badly. Satisfactory travel of material over the

deck was reached at about ½-in. stroke and, as will be seen by reference to Fig. 21, optimum conditions are indicated with a stroke somewhere between this and ⅝ inch.

TABLE 4.—*Specific-gravity Analyses of Table Discharges with Different Lengths of Stroke*

[For Explanation of Letters, see Table 1]

| Length of stroke, in... | ¼ | ⅜ | ½ | ⅝ | ¾ |
|---|---|---|---|---|---|
| Weight of sample, g... | 1000 | 1000 | 1000 | 1000 | 1000 |
| Calculated per cent. of feed +1.5 sp. gr.... | 15.18 | 16.70 | 15.21 | 16.37 | 13.17 |
| Position of center of mass of discharge in inches from feed end | 4.48 | 4.92 | 6.77 | 8.87 | 10.77 |

| Sample Mark | Sp. Gr. Classification | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_1$ | F | 408.4 | 357.8 | 87.7 | 415.2 | 376.2 | 90.7 | 300.6 | 290.8 | 96.9 | 159.0 | 153.1 | 96.5 | 75.6 | 72.1 | 95.5 |
| | $S_1$ | | 50.6 | | | 12.7 | | | 2.1 | | | 1.4 | | | 0.5 | |
| | $S_2$ | | | | | 26.3 | | | 7.7 | | | 4.5 | | | 3.0 | |
| $X_2$ | F | 319.3 | 267.9 | 83.9 | 260.1 | 226.4 | 87.0 | 205.3 | 197.1 | 96.0 | 153.7 | 143.7 | 93.5 | 90.3 | 86.7 | 96.0 |
| | $S_1$ | | 24.8 | | | 33.7 | | | 8.2 | | | 10.0 | | | 3.6 | |
| | $S_2$ | | 26.6 | | | | | | | | | | | | | |
| $X_3$ | F | 175.5 | 153.6 | 87.5 | 163.6 | 132.4 | 81.0 | 167.4 | 151.7 | 90.6 | 185.7 | 168.2 | 90.7 | 159.0 | 153.7 | 96.6 |
| | $S_1$ | | 21.9 | | | 7.9 | | | 4.6 | | | 6.1 | | | 1.5 | |
| | $S_2$ | | | | | 23.3 | | | 11.1 | | | 11.4 | | | 3.8 | |
| $X_4$ | F | 70.9 | 56.6 | 79.8 | 99.9 | 70.0 | 70.0 | 147.8 | 118.2 | 80.2 | 202.0 | 175.7 | 87.0 | 234.4 | 216.8 | 92.5 |
| | $S_1$ | | 2.6 | | | 29.9 | | | 29.6 | | | 26.3 | | | 17.6 | |
| | $S_2$ | | 11.7 | | | | | | | | | | | | | |
| $X_5$ | F | 19.2 | 10.1 | 52.6 | 52.7 | 25.5 | 48.4 | 123.7 | 76.7 | 62.0 | 190.0 | 147.7 | 77.7 | 258.0 | 218.7 | 84.8 |
| | $S_1$ | | .90 | | | 2.0 | | | 12.1 | | | 6.7 | | | 5.3 | |
| | $S_2$ | | 8.2 | | | 25.2 | | | 34.9 | | | 35.6 | | | 34.0 | |
| $X_6$ | F | 6.7 | 2.2 | 32.8 | 8.5 | 2.5 | 29.4 | 47.7 | 12.6 | 26.4 | 87.2 | 43.3 | 49.7 | 142.7 | 105.2 | 73.8 |
| | $S_1$ | | | | | 0.5 | | | 2.9 | | | 2.2 | | | 1.6 | |
| | $S_2$ | | 4.5 | | | 5.5 | | | 32.2 | | | 41.7 | | | 35.9 | |
| $X_7$ | F | No discharge so far along table. | | | | | | 7.5 | 0.8 | 10.7 | 22.4 | 4.6 | 20.5 | 40.0 | 15.1 | 37.8 |
| | $S_1$ | | | | | | | | 0.3 | | | 0.3 | | | 1.3 | |
| | $S_2$ | | | | | | | | 6.4 | | | 17.5 | | | 23.6 | |

Applying the same argument as to the upper convergence point of these curves as was applied to the similar set for air variation, convergence is indicated near abscissa 16.5, and the straight line portraying a uniform discharge rate along the coal side then falls between the curves for ½-in.

TABLE 5.—*Sizing Analyses of Table Discharges with Different Lengths of Stroke*

[For Explanation of Letters, see Table 1]

| Length of stroke, in. | | ¼ | | | ⅜ | | | ½ | | | ⅝ | | | ¾ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | |
| Size Group | | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | |
| $X_1$ | $F$ | 161.4 | 171.4 | 25.0 | 132.0 | 211.4 | 32.8 | 86.8 | 164.3 | 39.7 | 52.8 | 70.4 | 29.9 | 20.7 | 26.6 | 24.8 |
| | $S_1$ | 22.0 | | * | 10.4 | 2.3 | | 2.1 | | | 1.1 | 0.3 | | 0.5 | | |
| | $S_2$ | 16.0 | 12.0 | | 15.2 | 7.2 | 3.9 | | 2.6 | 5.1 | 0.7 | 0.7 | 3.1 | | 0.6 | 2.4 |
| $X_2$ | $F$ | 122.6 | 128.5 | 16.8 | 91.0 | 124.0 | 11.4 | 72.0 | 113.0 | 12.1 | 58.0 | 77.0 | 8.7 | 32.0 | 38.0 | 16.7 |
| | $S_1$ | 20.0 | 4.8 | | 9.0 | | * | 2.5 | | * | 2.7 | | * | 0.8 | | * |
| | $S_2$ | 13.8 | 9.7 | 3.1 | 14.0 | 7.0 | | 2.0 | 2.6 | | 4.5 | 1.0 | | | 0.7 | |
| $X_3$ | $F$ | 73.0 | 74.0 | 6.6 | 61.0 | 67.4 | 4.0 | 66.1 | 80.0 | 5.6 | 70.7 | 90.0 | 7.5 | 64.5 | 73.8 | 15.4 |
| | $S_1$ | 7.0 | | | 7.2 | 0.7 | | 4.3 | 0.3 | | 4.9 | 1.2 | | 1.1 | 0.4 | |
| | $S_2$ | 7.6 | 5.6 | | 13.8 | 7.1 | 2.4 | 7.3 | 2.7 | 1.1 | 7.8 | 2.0 | 1.6 | 1.7 | 0.9 | 1.2 |
| $X_4$ | $F$ | 28.9 | 26.3 | 1.4 | 33.0 | 34.0 | 3.0 | 58.0 | 56.2 | 4.0 | 76.0 | 94.7 | 5.0 | 95.0 | 112.0 | 9.8 |
| | $S_1$ | 2.6 | | | 4.0 | | * | 7.6 | | * | 6.7 | | * | 4.0 | | * |
| | $S_2$ | 5.6 | 5.2 | 0.9 | 14.0 | 10.0 | | 13.1 | 6.0 | | 13.0 | 5.0 | | 8.0 | 3.0 | |
| $X_5$ | $F$ | 5.0 | 4.7 | 0.4 | 12.0 | 12.1 | 0.4 | 42.9 | 32.1 | 1.7 | 62.6 | 80.8 | 4.3 | 97.3 | 113.8 | 7.6 |
| | $S_1$ | 0.90 | | | 1.6 | 0.4 | | 10.6 | 1.5 | | 6.1 | 0.6 | | 4.4 | 0.9 | |
| | $S_2$ | 5.1 | 2.9 | 0.2 | 12.5 | 11.5 | 1.2 | 19.6 | 12.6 | 2.7 | 20.9 | 11.9 | 2.8 | 25.1 | 6.9 | 2.0 |
| $X_6$ | $F$ | 1.4 | 0.8 | | 1.1 | 1.3 | 0.1 | 6.6 | 5.7 | 0.3 | 18.0 | 23.9 | 1.4 | 44.9 | 57.3 | 3.0 |
| | $S_1$ | | | | 0.5 | | | 2.4 | 0.5 | | 1.8 | 0.4 | | 0.7 | 0.9 | |
| | $S_2$ | 4.1 | 0.4 | | 3.3 | 2.1 | 0.1 | 18.1 | 12.3 | 1.8 | 23.4 | 15.7 | 2.6 | 19.7 | 14.1 | 2.1 |
| $X_7$ | $F$ | No discharge so far along table. | | | | | | 0.1 | 0.5 | 0.2 | 1.3 | 3.1 | 0.2 | 3.3 | 11.1 | 0.7 |
| | $S_1$ | | | | | | | 0.3 | | | 0.1 | 0.2 | | 0.4 | 0.9 | |
| | $S_2$ | | | | | | | 3.7 | 2.4 | 0.3 | 8.0 | 8.4 | 1.1 | 7.2 | 13.6 | 2.8 |

* These figures are calculated from the graphs

TABLE 6.—*Calculations for R. S. I.; Length of Stroke Variable*

| Length of stroke, in. | ¼ | ⅜ | ½ | ⅝ | ¾ |
|---|---|---|---|---|---|
| Total impurity in sample of 1000 g. | 151.8 | 167.0 | 152.1 | 163.7 | 131.7 |
| Impurity in coal, g. | 98.7 | 76.6 | 37.2 | 59.7 | 48.5 |
| Impurity in middling, g. | 25.2 | 43.9 | 51.8 | 45.9 | 39.1 |
| Impurity in slate, g. | 27.9 | 46.5 | 63.1 | 58.1 | 44.1 |
| Middling impurity allotted to coal, g. | 19.6 | 27.3 | 19.2 | 23.3 | 20.5 |
| Middling impurity allotted to slate, g. | 5.6 | 16.6 | 32.6 | 22.6 | 18.6 |
| Adjusted impurity in coal, g. | 118.3 | 103.9 | 56.4 | 83.0 | 69.0 |
| Adjusted impurity in slate, g. | 33.5 | 63.1 | 95.7 | 80.7 | 62.7 |
| R. S. I. | 22.1 | 37.7 | 62.8 | 49.3 | 47.6 |

and 5/8-in. strokes, thus indicating again the desirability of a uniform discharge rate.

The coal-content curves show a generally lower coal content in all products than is shown in Fig. 3. This is due to the fact that the air

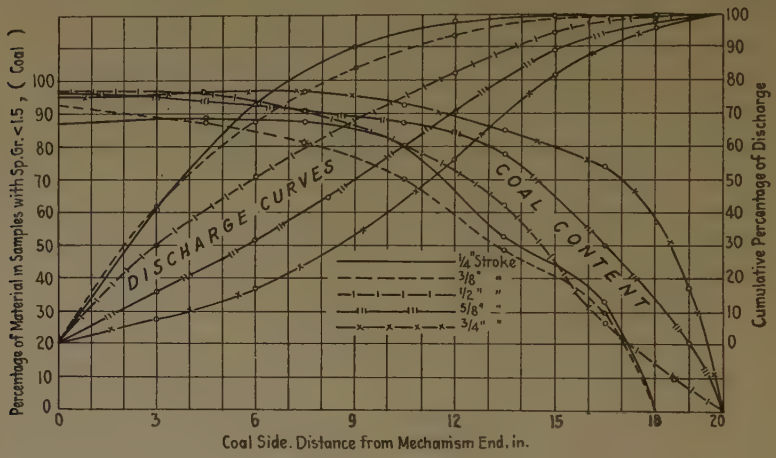


FIG. 14.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERENT LENGTHS OF STROKE.

supply was less than the optimum. Allowing for this general lowering, however, the discharges except those for the two lowest strokes held up fairly well in coal content until the midpoint of the discharge edge was passed. The bulk of this enriched product discharged, however, up to

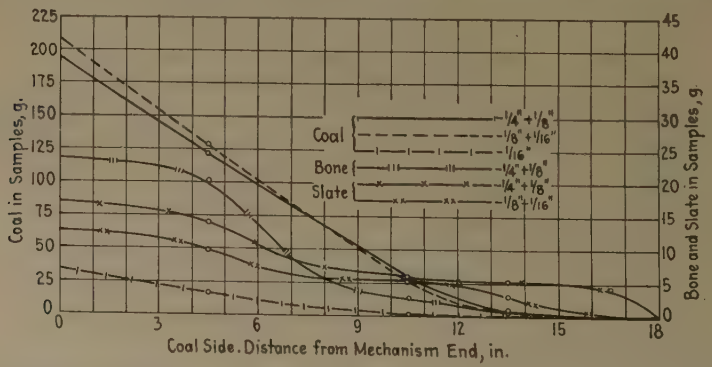


FIG. 15.—POSITION OF DISCHARGE WITH STROKE EQUAL TO 1/4 INCH.

this point was only 40 and 57 per cent. of the feed, for the two longer strokes, which made an excessive rejection. With 1/2-in. stroke 73 per cent. of the feed was discharged up to the midpoint and analyzed better than 90 per cent. coal, but the slate reject contained some material with nearly 60 per cent. coal content. With 5/8 and 3/4-in. strokes the longi-

tudinal travel was so rapid that coal was carried entirely too far toward the slate end of the table, while with ¼ and ⅜-in. strokes, the relatively low curvature of the coal-content graphs means correspondingly poor segregation of coal from slate. The ideal curve for this table would be one that was substantially horizontal for the first ⅔ to ¾ of the length

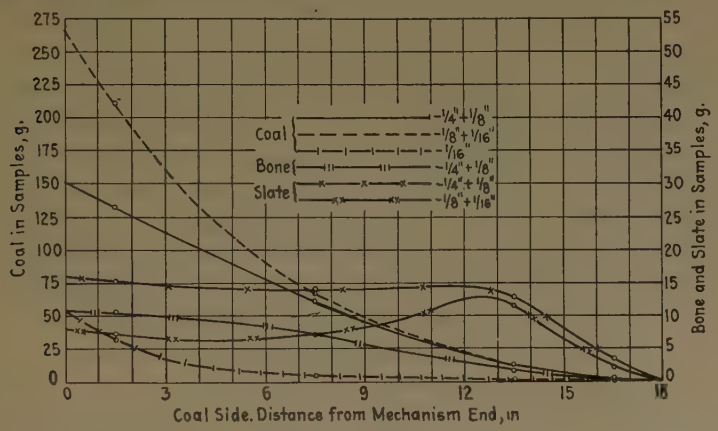


FIG. 16.—POSITION OF DISCHARGE WITH STROKE EQUAL TO ⅜ INCH.

of the graph, then dropped steeply nearly to the bottom of the sheet, and then ran, with a reverse curve, to the 20-in. mark. The curve for 12-in. stroke shows the nearest approach to these characteristics.

Fig. 15 shows, as was noted in discussing Fig. 14, substantially complete discharge of all products to the left of the midpoint, and while,

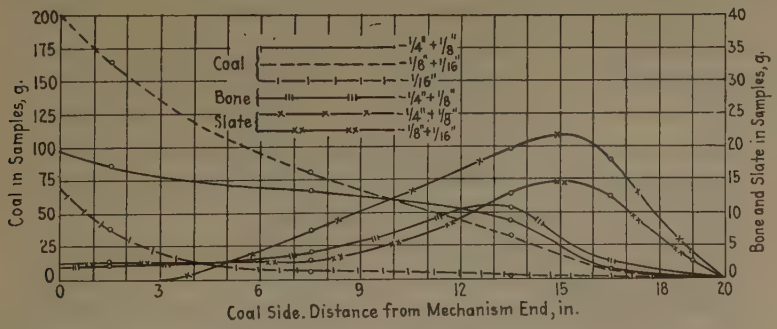


FIG. 17.—POSITION OF DISCHARGE WITH STROKE EQUAL TO ½ INCH.

reading the coal curves alone, satisfactory discharge is indicated, yet the curves show likewise maximum discharge of slate and bone in the first few inches of the table length, in other words, almost complete lack of separation. Fig. 16, with ⅜-in. stroke, shows the beginning of a movement toward separation. Coal discharge is still piled up at the mechanism end and the discharge rates of slate and bone at this end are

still entirely too large, but as compared with Fig. 15, the slate and bone discharges have moved distinctly to the right. It is interesting to note also that the curvature of the graphs for medium and fine coal is much steeper at the left-hand end of the plot than that for the coarse coal, indicating that stratification of the coal with fine on top has occurred. The curves for slate also show, by the peak in the curve for fine slate well

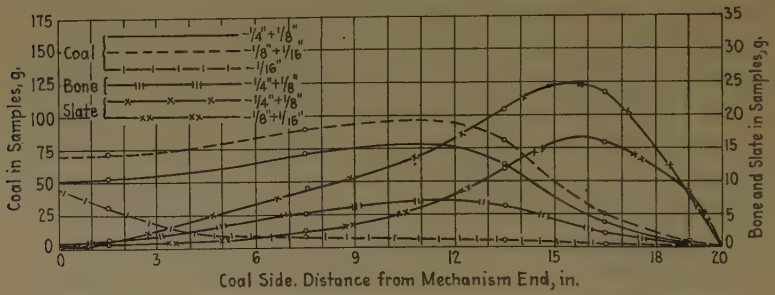


FIG. 18.—POSITION OF DISCHARGE WITH STROKE EQUAL TO 5/8 INCH.

to the right, that fine slate has settled to some extent below the coarse.

Fig. 17 shows satisfactory table operation. The coal is discharging at the maximum rate at the mechanism end and the bulk of the slate discharge has been transferred well toward the slate end. The peak in the bone curve comes near the valley formed by the coal and slate curves. The only objectionable feature in the curves is the appearance of fine slate and bone in the discharge from the first 3 inches.

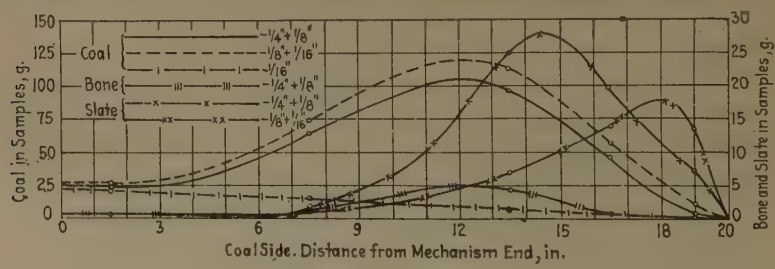


FIG. 19.—POSITION OF DISCHARGE WITH STROKE EQUAL TO 3/4 INCH.

Fig. 18 shows a drop in the rate of coal discharge near the mechanism end, as compared with Fig. 17, and while there is distinct betterment as regards discharge of fine slate and bone at this end, nevertheless the lack of a distinct valley indicates that the peak of efficient operation has been passed. Fig. 19 brings out clearly the fact that the impulse towards the slate end was too great. The peaks of coal and slate discharges have been moved close together and the effect on separation is much the same as that with the shortest stroke (see Fig. 15), the point of maximum discharge having been merely transferred from the mechanism end

to the slate end. It will be noted that the peak of the fine slate in this case has been displaced well to the right of the peak for coarse slate. The physical explanation for this is that with the increased stroke the bed near the slate end of the table was made markedly heavier and more sluggish with the result that the condition approximated closely that

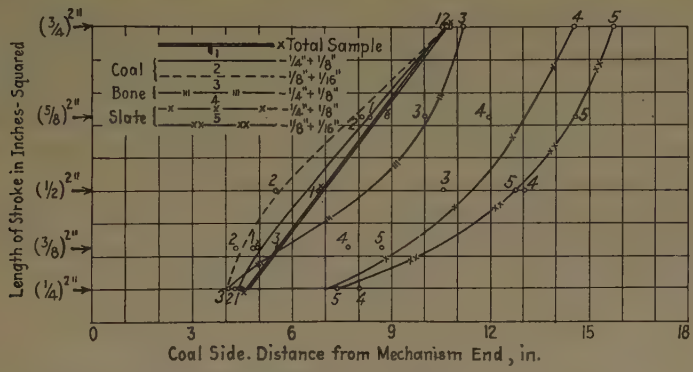


FIG. 20.—RELATION BETWEEN POSITIONS OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND LENGTH OF STROKE.

when a mixture of solids of different sizes is agitated in still air and stratification is on the basis of size alone.

Fig. 20 shows, by the same reasoning that was employed in discussing Fig. 12, maximum spacing between the mean coal and mean slate discharges about midway between ½ and ⅝-in. strokes and it is at this

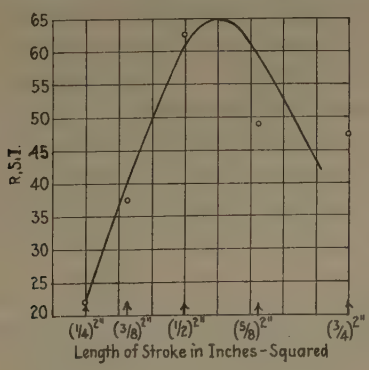


FIG. 21.—R. S. I.—STROKE.

position that maximum efficiency is indicated on the R. S. I. curve, Fig. 21.

It will be noted that the abscissas for Fig. 20 are the squares of the stroke length and that choice of this scale results in a straight line for the curve for total sample. This is because the travel of material across the table is made up of a succession of projectile-like movements and the

law governing such movement states the horizontal projection of the path to be proportional to the square of the initial velocity. This velocity varies, the speed being constant, with the length of stroke.

## General Observations on Stroke Length

Since no tests were run involving variations in size of feed, there are no data to establish the relation between this factor and stroke length. But since, in respect of longitudinal movement of the bed, at least, the conditions on the pneumatic table resemble those on the wet shaking table, the same rule should hold, *viz.*, that the stroke length should be increased with increase in size of material treated.

Stroke length and strokes per minute, being dependent factors in determining the velocity of the table top, are likewise dependent variables within the limits imposed on stroke length by feed size.

## Effect of Variation in Speed

In this series of tests air supply was held constant at 322 cu. ft. per min.; stroke length, ½ in.; longitudinal slope, ⅝ in. per ft.; transverse slope, 3½ in. per ft.; rocker-arm angle, 17½°, and speed varied from 222 to 450 strokes per min. The feed rate was about 3100 g. per minute.

The experimental results are tabulated in Tables 7 and 8, and the calculations leading up to R. S. I. in Table 9.

The cumulative discharge curves on Fig. 22 show that with 222 strokes per min., 90 per cent. of the feed discharged within the first 7½ in. from the mechanism end. Physically interpreted this means that there was a thick sluggish bed which traveled directly down the table from feed to discharge with no chance for effective segregation therein. At 300 and 330 strokes per min. the material was much better distributed, but even here 90 per cent. of the material was discharged in 70 per cent. of the length of the table. The most effective speed was 390 strokes per min., and the curve for this speed averages nearest the straight line portraying uniform discharge.

Reading the discharge curve for 390 strokes per min. in connection with the corresponding coal-content curve, we find that at 16½ in., where 90 per cent. of the material has been discharged, the percentage of coal in the slate is 55, with a relatively rapid drop to zero in the next 3½ in. Comparing this with the curves for 450 strokes per min., while it appears that in the latter case the material was even more thinly spread on the table and at the 90 per cent. point on the cumulative curve the percentage of coal in the discharge was only 52½ per cent., yet the grade of material discharging in the first 6 in. was distinctly lower than that at 390 strokes per minute.

TABLE 7.—*Specific-gravity Analyses of Table Discharges at Different Speeds*

[For Explanation of Letters, see Table 1]

| Speed, r.p.m. | 222 | | | 300 | | | 330 | | | 390 | | | 450 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight of sample, g. | 1000 | | | 1000 | | | 1000 | | | 1000 | | | 1000 | | |
| Calculated percentage of feed +1.5 sp. gr. | 13.35 | | | 14.03 | | | 15.87 | | | 14.07 | | | 16.55 | | |
| Position of center of mass of discharge in inches from feed end | 3.38 | | | 6.95 | | | 7.25 | | | 10.53 | | | 13.33 | | |
| Sample Mark | Sp. Gr. Classification | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages |
| $X_1$ | $F$ | 613.7 | 546.8 | 89.2 | 260.7 | 249.2 | 95.6 | 256.4 | 246.7 | 96.2 | 87.2 | 84.5 | 97.0 | 33.1 | 31.3 | 94.5 |
| | $S_1$ | | 17.1 | | | 6.6 | | | 4.1 | | | 2.7 | | | 0.1 | |
| | $S_2$ | | 49.8 | | | 4.9 | | | 5.6 | | | | | | 1.7 | |
| $X_2$ | $F$ | 215.4 | 188.4 | 87.6 | 222.7 | 207.4 | 93.0 | 196.0 | 185.7 | 94.7 | 95.5 | 92.6 | 97.0 | 20.8 | 20.0 | 96.2 |
| | $S_1$ | | 3.9 | | | 15.3 | | | 10.3 | | | 2.9 | | | 0.8 | |
| | $S_2$ | | 23.1 | | | | | | | | | | | | | |
| $X_3$ | $F$ | 117.6 | 94.9 | 80.7 | 186.0 | 168.4 | 90.6 | 186.4 | 172.3 | 92.6 | 157.6 | 152.8 | 97.0 | 68.8 | 67.0 | 97.4 |
| | $S_1$ | | 4.4 | | | 4.4 | | | 8.3 | | | 3.4 | | | 0.7 | |
| | $S_2$ | | 18.3 | | | 13.2 | | | 5.8 | | | 1.4 | | | 1.1 | |
| $X_4$ | $F$ | 37.1 | 27.0 | 72.8 | 156.3 | 135.9 | 87.0 | 166.2 | 138.8 | 83.5 | 236.6 | 227.2 | 96.0 | 192.5 | 184.8 | 96.0 |
| | $S_1$ | | 1.5 | | | 20.4 | | | 27.4 | | | 9.4 | | | 7.7 | |
| | $S_2$ | | 8.6 | | | | | | | | | | | | | |
| $X_5$ | $F$ | 16.2 | 9.4 | 58.0 | 126.1 | 86.9 | 68.9 | 134.3 | 84.8 | 63.2 | 250.5 | 220.8 | 88.2 | 319.1 | 301.6 | 94.5 |
| | $S_1$ | | 1.1 | | | 10.6 | | | 7.4 | | | 14.2 | | | 8.7 | |
| | $S_2$ | | 5.7 | | | 28.6 | | | 42.1 | | | 15.5 | | | 8.8 | |
| $X_6$ | $F$ | No discharge so far. | | | 37.6 | 10.4 | 27.7 | 50.7 | 12.1 | 23.9 | 133.4 | 74.3 | 55.7 | 251.0 | 194.6 | 77.5 |
| | $S_1$ | | | | | 1.4 | | | 1.6 | | | 10.6 | | | 17.0 | |
| | $S_2$ | | | | | 25.8 | | | 37.0 | | | 48.5 | | | 39.4 | |
| $X_7$ | $F$ | | | | 10.6 | 1.5 | 14.1 | 10.0 | 0.9 | 9.0 | 39.1 | 7.0 | 17.9 | 93.5 | 33.3 | 35.6 |
| | $S_1$ | | | | | | | | | | | 2.5 | | | 4.5 | |
| | $S_2$ | | | | | 9.1 | | | 9.1 | | | 29.6 | | | 55.7 | |
| $X_8$ Discharge over end of table. | $F$ | Discharge over end of table ——→ | | | | | | | | | | | | 21.2 | 1 9 | 8.9 |
| | $S_1$ | | | | | | | | | | | | | | 0.4 | |
| | $S_2$ | | | | | | | | | | | | | | 18.9 | |

TABLE 8.—*Sizing Analyses of Table Discharges at Different Speeds*

[For Explanation of Letters, see Table 1]

| Speed, r. p. m. | | 222 | | | 300 | | | 330 | | | 390 | | | 450 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | | Weight, G. | | |
| Size Group | | −¼" +⅛" | −⅛" +1/16" | −1/16" | −¼" +⅛" | −⅛" +1/16" | −1/16" | −¼" +⅛" | −⅛" +1/16" | −1/16" | −¼" +⅛" | −⅛" +1/16" | −1/16" | −¼" +⅛" | −⅛" +1/16" | −1/16" |
| $X_1$ | $F$ | 232.6 | 292.4 | 21.8 | 98.5 | 129.8 | 23.9 | 106.1 | 110.3 | 30.3 | 11.3 | 52.3 | 20.9 | 0.3 | 12.2 | 18.8 |
| | $S_1$ | 14.2 | 2.9 | | 4.8 | 1.6 | 0.2 | 3.2 | 0.8 | 0.1 | 0.3 | 0.1 | | 0.1 | | |
| | $S_2$ | 20.0 | 24.3 | 5.5 | 2.2 | 1.2 | 1.5 | 1.3 | 1.1 | 3.2 | 0.1 | 0.3 | 1.9 | | 0.1 | 1 . |
| $X_2$ | $F$ | 78.2 | 96.4 | 13.8 | 92.0 | 105.0 | 10.4 | 80.0 | 93.7 | 12.0 | 30.0 | 54.6 | 8.0 | 2.0 | 7.0 | 11.0 |
| | $S_1$ | 1.8 | 2.1 | | 4.5 | | * | 3.5 | | * | 1.5 | | * | | | * |
| | $S_2$ | 13.8 | 6.8 | 2.5 | 6.5 | 2.0 | | 1.3 | 2.0 | | 0.2 | 0.3 | | | | |
| $X_3$ | $F$ | 45.4 | 46.3 | 3.2 | 78.5 | 84.4 | 5.5 | 73.2 | 91.2 | 7.9 | 64.4 | 81.3 | 7.1 | 14.3 | 42.3 | 10.4 |
| | $S_1$ | 3.8 | 0.6 | | 3.2 | 1.0 | 0.2 | 6.5 | 1.3 | 0.5 | 2.6 | 0.7 | 0.1 | | 0.3 | 0.4 |
| | $S_2$ | 12.2 | 5.3 | 0.8 | 8.9 | 3.2 | 1.1 | 1.4 | 3.2 | 1.2 | 0.4 | 0.4 | 0.6 | | 0.1 | 1.0 |
| $X_4$ | $F$ | 8.3 | 16.6 | 2.1 | 69.0 | 65.0 | 1.9 | 60.0 | 73.0 | 5.8 | 100.0 | 122.0 | 5.2 | 62.0 | 113.0 | 9.8 |
| | $S_1$ | 1.2 | 0.3 | | 2.5 | | * | 10.0 | | * | 4.0 | | * | 2.0 | | * |
| | $S_2$ | 4.0 | 3.9 | 0.7 | 10.8 | 6.0 | | 8.0 | 6.5 | | 1.2 | 1.0 | | 1.0 | 1.5 | |
| $X_5$ | $F$ | 4.5 | 4.5 | 0.4 | 49.7 | 35.5 | 1.7 | 35.8 | 46.4 | 2.6 | 102.5 | 115.0 | 3.3 | 149.1 | 144.0 | 8.5 |
| | $S_1$ | 0.8 | 0.3 | | 8.3 | 2.2 | 0.1 | 5.9 | 1.3 | 0.2 | 11.6 | 2.4 | 0.2 | 5.7 | 2.5 | 0.5 |
| | $S_2$ | 3.2 | 2.0 | 0.5 | 15.1 | 11.7 | 1.8 | 23.0 | 16.4 | 2.7 | 8.2 | 5.6 | 1.7 | 3.3 | 3.2 | 2.3 |
| $X_6$ | $F$ | No discharge so far. | | | 5.0 | 5.1 | 0.3 | 5.2 | 6.4 | 0.5 | 34.2 | 38.4 | 1.7 | 90.2 | 101.2 | 3.2 |
| | $S_1$ | | | | 0.9 | 0.5 | | 0.9 | 0.6 | 0.1 | 8.7 | 1.5 | 0.4 | 12.2 | 3.8 | 1.0 |
| | $S_2$ | | | | 16.3 | 8.5 | 1.0 | 20.6 | 14.8 | 1.6 | 29.7 | 16.2 | 2.6 | 27.2 | 9.5 | 2.7 |
| $X_7$ | $F$ | | | | 0.8 | 0.6 | 0.1 | 0.2 | 0.6 | 0.1 | 2.4 | 4.4 | 0.2 | 15.5 | 17.2 | 0.6 |
| | $S_1$ | | | | | | | | | | 1.5 | 0.9 | 0.1 | 2.3 | 2.1 | 0.1 |
| | $S_2$ | | | | 6.3 | 2.6 | 0.2 | 5.1 | 3.7 | 0.3 | 13.0 | 14.9 | 1.7 | 29.9 | 23.5 | 2.3 |
| $X_8$ | $F$ | Discharge over end of table ⟶ | | | | | | | | | | | | 0.4 | 1.3 | 0.2 |
| | $S_1$ | | | | | | | | | | | | | 0.2 | 0.2 | |
| | $S_2$ | | | | | | | | | | | | | 8.3 | 9.2 | 1.4 |

* These figures are calculated from graphs.

TABLE 9.—*Calculations for R. S. I.; Speed the Variable*

| Speed, r.p.m. | 222 | 300 | 330 | 390 | 450 |
|---|---|---|---|---|---|
| Total impurity in sample of 1000 g. | 133.5 | 140.3 | 158.7 | 140.7 | 165.5 |
| Impurity in coal, g. | 77.3 | 47.8 | 42.4 | 30.7 | 38.3 |
| Impurity in middling, g. | 29.6 | 35.1 | 49.5 | 44.1 | 55.2 |
| Impurity in slate, g. | 26.6 | 57.4 | 66.8 | 65.9 | 72.0 |
| Middling impurity allotted to coal, g. | 22.9 | 15.9 | 19.2 | 14.0 | 19.2 |
| Middling impurity allotted to slate, g. | 6.7 | 19.2 | 30.3 | 30.1 | 36.0 |
| Adjusted impurity in coal, g. | 100.2 | 63.7 | 61.6 | 44.7 | 57.5 |
| Adjusted impurity in slate, g. | 33.3 | 76.6 | 97.1 | 96.0 | 108.0 |
| R. S. I. | 25.0 | 54.6 | 61.2 | 68.3 | 65.3 |

Fig. 23 shows the coal not properly stratified. Coarse coal discharged before the fine, which means that it was on top. The reason for this was that the bed was so thick and sluggish at this low speed that the air

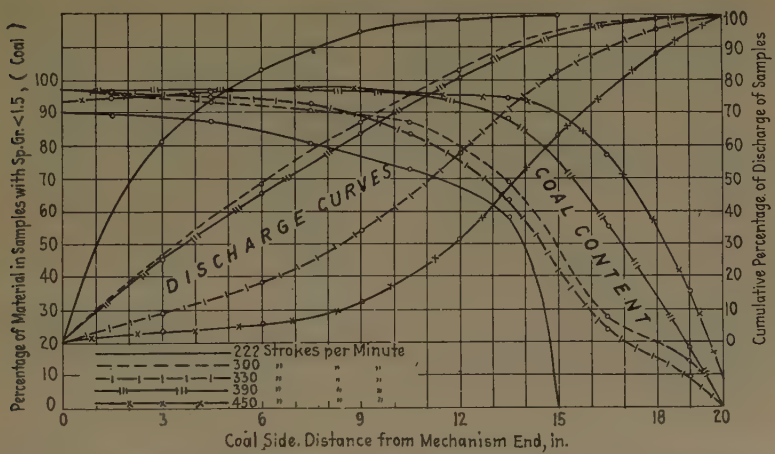


FIG. 22.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERENT SPEEDS.

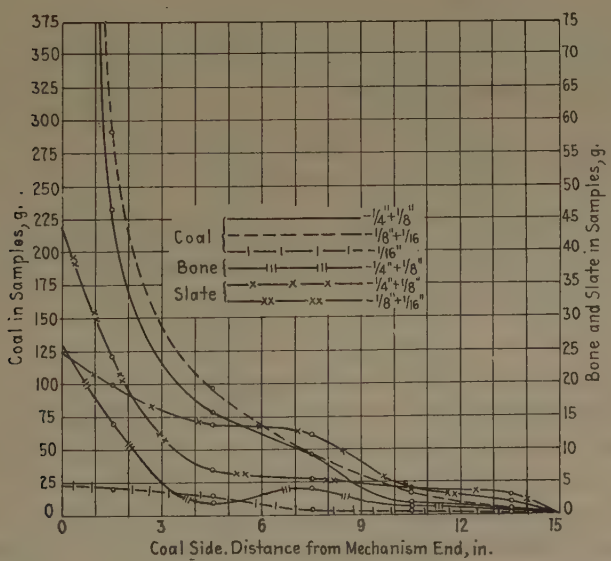


FIG. 23.—POSITION OF DISCHARGE WITH SPEED EQUAL TO 222 STROKES PER MINUTE.

could not effect proper suspension of the particles and that stratification took place, therefore, according to the laws applying when agitation unaccompanied by effective buoyant action of the surrounding fluid is applied to a mass of grains of mixed sizes.

Fig. 24 (300 strokes per min.) shows a distinct beginning of concentration, coal discharging in bulk toward the head end of the table and the bulk of slate toward the slate end, but the gradual rise of the slate curves

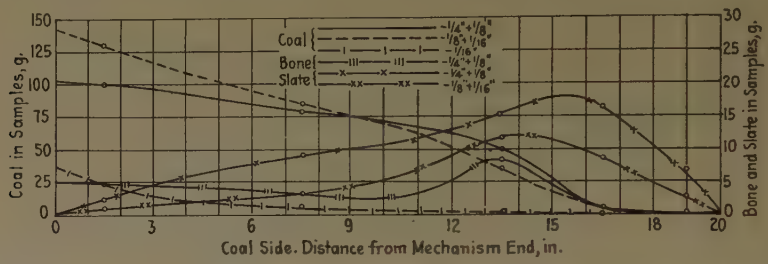


FIG. 24.—POSITION OF DISCHARGE WITH SPEED EQUAL TO 300 STROKES PER MINUTE.

and gradual fall of the coal curves are not those indicating efficient concentration. The curves on Fig. 25 (330 strokes per min.) show little change in position of discharge of the coal due to the increase in speed,

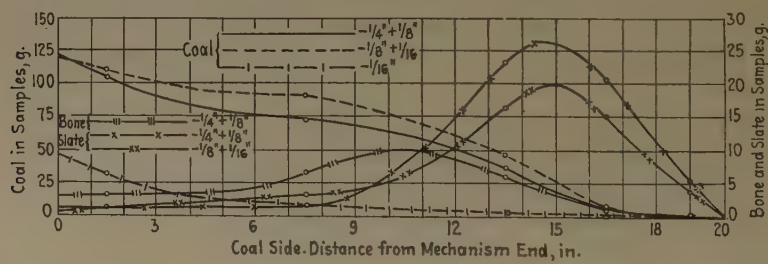


FIG. 25.—POSITION OF DISCHARGE WITH SPEED EQUAL TO 330 STROKES PER MINUTE.

but distinct retardation of slate discharge until the midpoint of the discharge edge is reached. In Fig. 26 (390 strokes per min.) representing optimum conditions, intermediate and fine coal were well above the

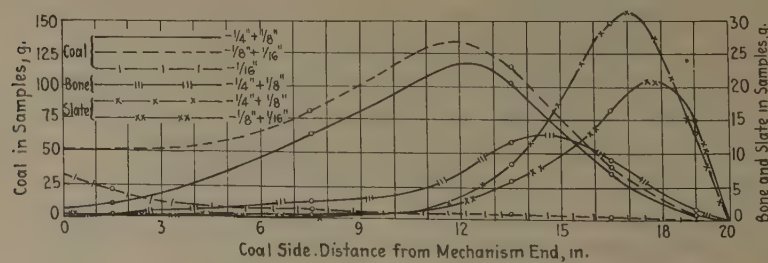


FIG. 26.—POSITION OF DISCHARGE WITH SPEED EQUAL TO 390 STROKES PER MINUTE.

coarse, as is shown by the positions of their respective curves at the left-hand edge of the table; slate and bone were well stratified, as indicated by the way in which the curves for these substances hug the lower line of the

chart; the point of maximum discharge of coal, *viz.:* about 12 in. from the mechanism end, was well separated from that of slate at slightly over 17 in.; and the slate-discharge curves make pronounced peaks with steeply sloping sides, which means that slate discharge was distinctly segregated to the last 5 in. of the table. The valley between the slate and coal curves is deep, and the bone curve shows its peak in the ideal

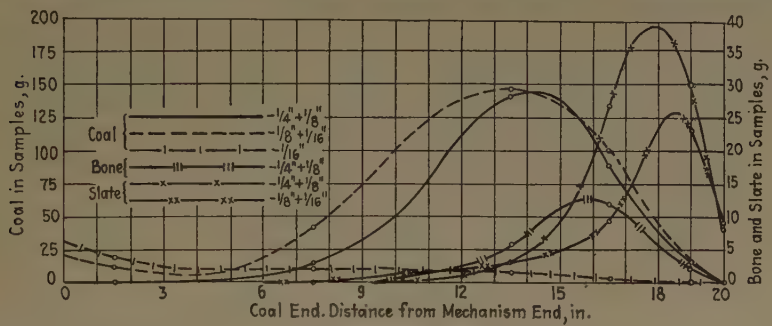


FIG. 27.—POSITION OF DISCHARGE WITH SPEED EQUAL TO 450 STROKES PER MINUTE.

position, *i. e.*, in this valley. Fig. 27 shows the whole discharge moved over toward the slate end, some of it even moving around onto the slate end. The peaks of the slate and coal curves are crowded together some 20 to 25 per cent. as compared to the preceding operation, thereby making a more difficult separation.

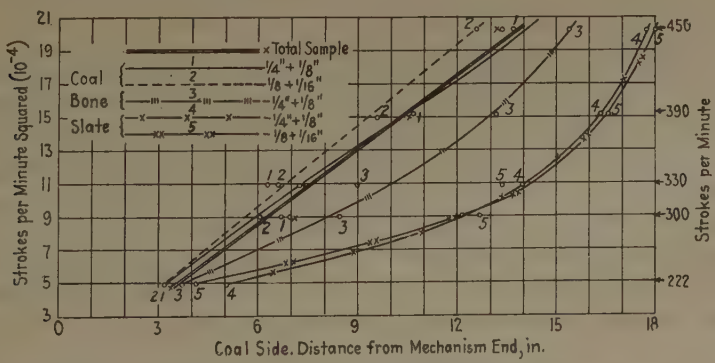


FIG. 28.—RELATION BETWEEN POSITIONS OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND SPEED.

Fig. 28 shows a substantially straight-line movement, along the discharge edge, of the center of mass of the whole bed with increase in the square of the number of strokes per minute, and substantially the same variation for coal. The center of mass of the slate discharge moves toward the slate end at a greater rate throughout the first part of the speed range investigated and thereafter at a lesser rate.

The existence of a straight-line relationship between the square of the speed and the travel of the material here indicated leads to the conclusion that the travel is due to a succession of projectile-like paths, the usual formula for the horizontal range $R$ being $R = \frac{V^2 \sin 2\theta}{g}$, where $V$ is the initial velocity, $\theta$ the angle of elevation of the initial path from the horizontal and $g$ the gravitational unit.

Fig. 28 also shows that maximum divergence of the mean coal and mean slate curves comes at slightly more than 330 strokes per min., which is thereby indicated as the point at which table operation would be easiest. Fig. 29, on the other hand, indicates a maximum R. S. I. at or slightly above 390 strokes per min. Reference back to the text

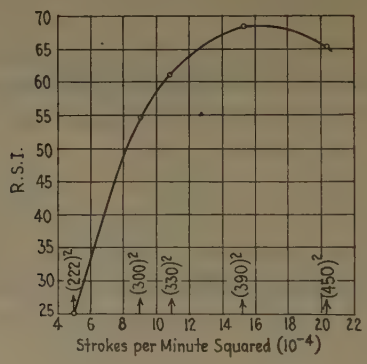


FIG. 29.—R. S. I.—SPEED.

dealing with Figs. 25 and 26 and to the figures themselves shows that the superior results in the run at 390 strokes per min. are due to the way in which slate discharge has been held back until close to the slate end of the deck and to a corresponding retardation of bone. Thus while the coal discharge as a whole is shown moved to the right in Fig. 26 as compared to Fig. 25, and thereby moved closer to the center of the slate discharge, as Fig. 28 shows, yet Fig. 26, with its steep-sided valley and the bone peak well to the right of the coal, indicates conditions that permit a good cut, and the coal is exceptionally clean.

## General Observations on Speed

As noted under stroke length, this variable and speed are dependent, high speed being a necessary accompaniment of short stroke and *vice versa*. Figs. 26, 27 and 28 compared with the two preceding them and with the similar groups portraying the effects of the other variables, indicate that the bunching together of different constituents of a feed, as shown by the sharpness of the peaks, is more greatly affected by this variable than by any of the others investigated.

## Effect of Change in Longitudinal Slope

Tables 10 and 11 present the experimental data in a series of tests in which longitudinal slope varied from ⅜ to 1⅜ in. per ft. while the other variables were kept constant at the following figures: air supply, 375 cu. ft. per min.; length of stroke, ½ in.; strokes per min., 390; transverse slope, 3½ in. per ft.; rocker-arm angle, 17½°. The feed rate was about 3200 g. per min. Table 12 shows the calculations for values of R. S. I.

Table 10.—*Specific-gravity Analyses of Table Discharges with Differing Longitudinal Slope*

[For Explanation of Letters, see Table 1]

| Angle of slope | | 1° 30′ | | | 2° 45′ | | | 4° 30′ | | | 6° 15′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight of sample, g. | | 1000 | | | 1000 | | | 1000 | | | 1000 | | |
| Calculated percentage of feed +1.5 sp. gr. | | 17.98 | | | 12.21 | | | 15.59 | | | 14.81 | | |
| Position of center of mass of discharge in inches from feed end | | 13.90 | | | 8.66 | | | 3.82 | | | 1.91 | | |
| Sample Mark | Sp. Gr. Classification | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages |
| $X_1$ | $F$ | 25.9 | 25.3 | 97.6 | 187.6 | 183.2 | 97.7 | 582.0 | 546.7 | 94.0 | 871.6 | 779.0 | 89.4 |
| | $S_1$ | | 0.1 | | | 1.9 | | | 19.9 | | | 24.5 | |
| | $S_2$ | | 0.5 | | | 2.5 | | | 15.4 | | | 68.1 | |
| $X_2$ | $F$ | 31.7 | 30.8 | 97.3 | 147.6 | 143.2 | 97.0 | 210.0 | 186.6 | 88.8 | 120.8 | 71.1 | 58.8 |
| | $S_1$ | | 0.9 | | | 4.4 | | | 23.4 | | | 5.2 | |
| | $S_2$ | | | | | | | | | | | 44.5 | |
| $X_3$ | $F$ | 69.7 | 67.6 | 97.0 | 166.0 | 159.4 | 96.0 | 107.0 | 82.6 | 77.2 | 5.3 | 1.8 | 34.0 |
| | $S_1$ | | 1.1 | | | 4.1 | | | 9.5 | | | | |
| | $S_2$ | | 1.0 | | | 2.5 | | | 14.9 | | | 3.5 | |
| $X_4$ | $F$ | 143.1 | 136.8 | 95.6 | 199.2 | 184.3 | 92.5 | 60.8 | 26.0 | 42.8 | 2.3 | 2.3 | |
| | $S_1$ | | 6.3 | | | 14.9 | | | 34.8 | | | | |
| | $S_2$ | | | | | | | | | | | | |
| $X_5$ | $F$ | 286.0 | 264,5 | 92.4 | 200.4 | 164.8 | 82.2 | 34.9 | 2.2 | 6.3 | | | |
| | $S_1$ | | 11.7 | | | 15.6 | | | 1.2 | | | | |
| | $S_2$ | | 9.8 | | | 20.0 | | | 31.5 | | | | |
| $X_6$ | $F$ | 252.0 | 206.2 | 81.8 | 84.4 | 41.3 | 48.9 | 5.3 | | | | | |
| | $S_1$ | | 25.1 | | | 6.3 | | | | | | | |
| | $S_2$ | | 20.7 | | | 36.8 | | | 5.3 | | | | |
| $X_7$ | $F$ | 152.1 | 81.4 | 53.5 | 14.8 | 1.7 | 11.5 | No discharge so far along table. | | | | | |
| | $S_1$ | | 14.7 | | | 0.2 | | | | | | | |
| | $S_2$ | | 56.0 | | | 12.9 | | | | | | | |
| $X_8$ | $F$ | 39.5 | 7.6 | 19.2 | ←——Discharge over end of table | | | | | | | | |
| | $S_1$ | | 1.7 | | | | | | | | | | |
| | $S_2$ | | 30.2 | | | | | | | | | | |

TABLE 11.—*Sizing Analyses of Table Discharges with Differing Longitudinal Slope*

[For Explanation of Letters, see Table 1]

| Longitudinal slope | | 1° 30′ | | | 2° 45′ | | | 4° 30′ | | | 6° 15′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Size Group | | Weights of Sp. Gr.-Size Groups in Grams | | | | | | | | | | | |
| | | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ |
| $X_1$ | $F$ | 0.5 | 16.3 | 8.5 | 40.0 | 117.2 | 26.0 | 236.0 | 272.0 | 38.7 | 414.2 | 333.0 | 31.8 |
| | $S_1$ | | 0.1 | | 1.0 | 0.5 | 0.4 | 15.1 | 4.1 | 0.7 | 17.2 | 6.8 | 0.5 |
| | $S_2$ | | 0.1 | 0.4 | 0.7 | 1.2 | 0.6 | 4.4 | 6.2 | 4.8 | 41.5 | 21.1 | 5.5 |
| $X_2$ | $F$ | 3.8 | 22.0 | 5.0 | 61.0 | 76.2 | 6.0 | 120.0 | 58.6 | 8.0 | 40.8 | 28.2 | 2.1 |
| | $S_1$ | | | * | 1.5 | | * | 12.0 | | * | 3.8 | 1.3 | 0.1 |
| | $S_2$ | | 0.3 | | 0.8 | 1.1 | | 5.0 | 5.0 | | 32.8 | 10.5 | 1.2 |
| $X_3$ | $F$ | 11.6 | 52.5 | 3.5 | 82.4 | 73.0 | 4.0 | 59.0 | 22.6 | 1.0 | | 1.8 | |
| | $S_1$ | 0.3 | 0.7 | 0.1 | 2.8 | 1.0 | 0.3 | 8.6 | 0.8 | 0.1 | | | |
| | $S_2$ | | 0.6 | 0.4 | 1.0 | 1.2 | 0.3 | 8.5 | 5.5 | 0.9 | 2.0 | 1.0 | 0.5 |
| $X_4$ | $F$ | 50.0 | 83.4 | 3.4 | 109.0 | 72.3 | 3.0 | 19.0 | 7.0 | | | | |
| | $S_1$ | 1.5 | | * | 7.5 | | * | 4.5 | | * | | | |
| | $S_2$ | 1.5 | 1.5 | | 3.2 | 2.0 | | 19.5 | 7.8 | | 1.5 | 0.6 | 0.2 |
| $X_5$ | $F$ | 175.2 | 86.0 | 3.3 | 100.0 | 63.3 | 1.5 | 1.0 | 1.1 | 0.1 | | | |
| | $S_1$ | 10.1 | 1.3 | 0.3 | 10.7 | 1.5 | 0.4 | 1.1 | 0.1 | | | | |
| | $S_2$ | 6.0 | 3.1 | 0.7 | 13.0 | 8.8 | 1.2 | 23.6 | 7.2 | 0.7 | | | |
| $X_6$ | $F$ | 155.3 | 49.5 | 1.4 | 32.0 | 8.5 | 0.8 | | | | | | |
| | $S_1$ | 23.8 | 1.1 | 0.2 | 4.8 | 1.3 | 0.2 | | | | | | |
| | $S_2$ | 14.5 | 5.6 | 0.6 | 25.4 | 10.4 | 1.0 | 3.7 | 1.5 | 0.1 | | | |
| $X_7$ | $F$ | 63.6 | 17.1 | 0.7 | 1.0 | 0.6 | 0.1 | No discharge so far along table. | | | | | |
| | $S_1$ | 13.2 | 1.3 | 0.2 | 0.2 | | | | | | | | |
| | $S_2$ | 44.8 | 10.1 | 1.1 | 7.4 | 5.2 | 0.3 | | | | | | |
| $X_8$ | $F$ | 5.9 | 1.4 | 0.3 | ←——Discharge over end of table. | | | | | | | | |
| | $S_1$ | 1.4 | 0.3 | | | | | | | | | | |
| | $S_2$ | 23.3 | 6.5 | 0.4 | | | | | | | | | |

* These figures are calculated from the graphs.

TABLE 12.—*Calculations for R. S. I.; Longitudinal Slope the Variable*

| Longitudinal slope, deg | 1° 30′ | 2° 45′ | 4° 30′ | 6° 15′ |
|---|---|---|---|---|
| Longitudinal slope, in. per ft | 0.31 | 0.58 | 0.94 | 1.31 |
| Total impurity in sample of 1000 g | 179.8 | 122.1 | 155.9 | 148.1 |
| Impurity in coal, g | 50.9 | 30.2 | 46.4 | 57.1 |
| Impurity in middling, g | 63.9 | 35.2 | 36.7 | 43.5 |
| Impurity in slate, g | 65.0 | 56.5 | 72.8 | 47.5 |
| Middling impurity allotted to coal, g | 28.1 | 12.3 | 14.3 | 23.7 |
| Middling impurity allotted to slate, g | 35.8 | 22.9 | 22.4 | 19.8 |
| Adjusted impurity in coal, g | 79.0 | 42.5 | 60.7 | 80.8 |
| Adjusted impurity in slate, g | 100.8 | 79.4 | 95.2 | 67.3 |
| R. S. I. | 56.0 | 65.2 | 61.0 | 45.4 |

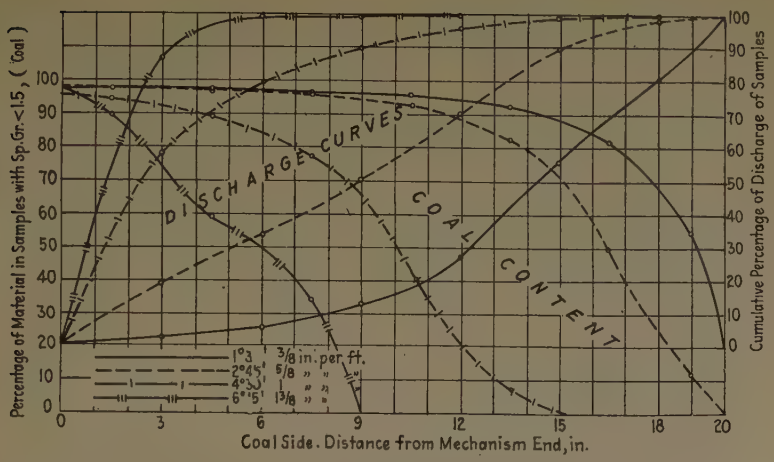


FIG. 30.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERING LONGITUDINAL SLOPE.

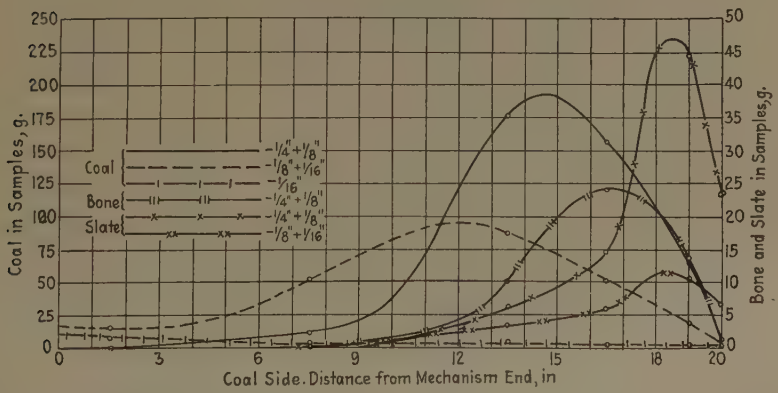


FIG. 31.—POSITION OF DISCHARGE WITH LONGITUDINAL SLOPE EQUAL TO 1° 30′.

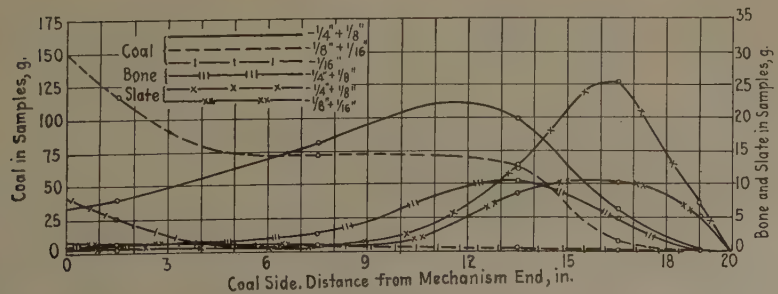


FIG 32.—POSITION OF DISCHARGE WITH LONGITUDINAL SLOPE EQUAL TO 2° 45′.

The discharge curves on Fig. 30 show that with small longitudinal slope discharge is slow in starting and that at the midpoint of the table's

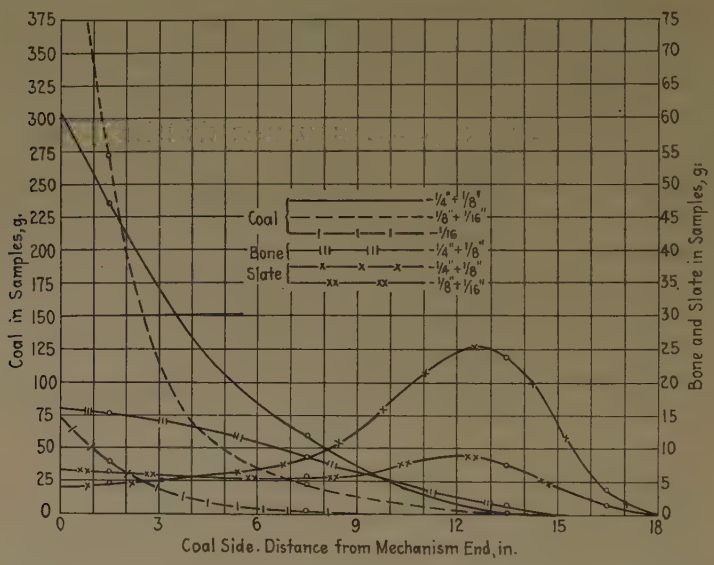


FIG. 33.—POSITION OF DISCHARGE WITH LONGITUDINAL SLOPE EQUAL TO 4° 30′.

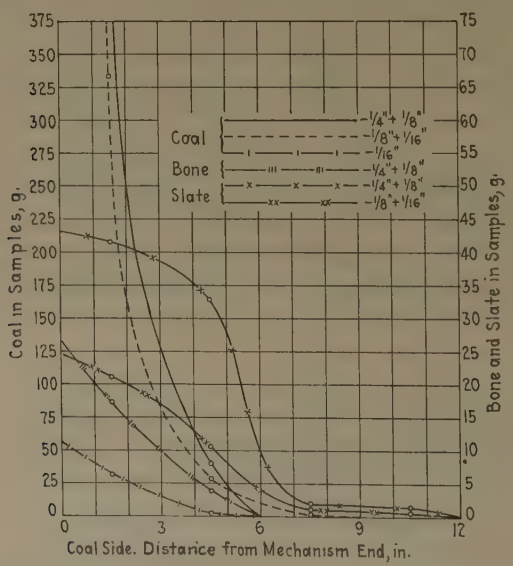


FIG. 34.—POSITION OF DISCHARGE WITH LONGITUDINAL SLOPE EQUAL TO 6° 15′.

length only 15 per cent. of the material has been discharged. With maximum slope, substantially 90 per cent. of the total feed to the table

is discharged within the first 3 in. As in preceding series, optimum conditions were obtained when the discharge was most nearly uniform, which was with a slope of ⅝ in. per ft. With this slope, 90 per cent. of the material was discharged in the first 15 in., and the slate discharge at this point had some 72 per cent. of coal, but the coal content from there on dropped quickly.

Fig. 31 shows the coal properly stratified, the slate-discharge curves with properly steeply sloping sides indicating a desirable compression of the slate discharge area, and the peak of the bone generally in the valley between the slate and coal curves, but the whole discharge, and

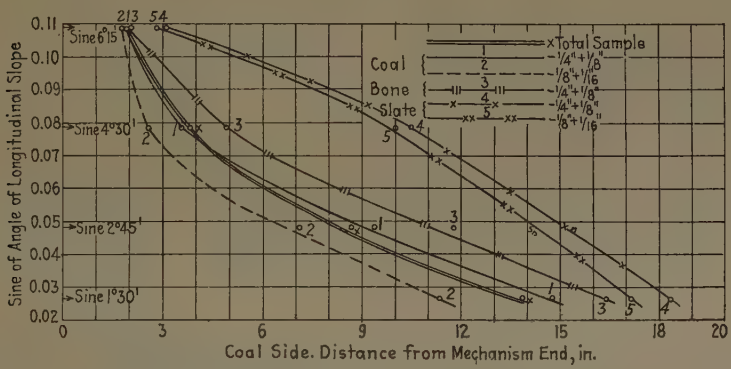


FIG. 35.—RELATION BETWEEN POSITIONS OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND LONGITUDINAL SLOPE.

particularly that of the coarse coal, is moved so far to the right as to prevent proper separation. Fig. 32, on the contrary, shows a distinctly more favorable condition, with the coal discharging at a good rate near the mechanism end of the table and slate discharge, although beginning at the mechanism end, yet remaining fairly low until past the midpoint. Fig. 33 shows the beginning of crowding of the products toward the mechanism end, and while there is a relatively great spread between the points of maximum discharge of coal and slate, yet the discharge rate of the slate at the mechanism end is distinctly too high and a large part of the bone is thrown into the coal. Fig. 34 shows the condition of crowding at the mechanism end in aggravated form with corresponding failure to effect any separation.

Fig. 36 shows the only marked variation found in any of the tests from the rule that the movement of the center of mass of the discharging material along the coal side is a straight-line function of the variable under investigation or of some easily recognizable function thereof. Here the curve for the whole mass would indicate that this movement is affected most by given changes in slope when the slope is least, and conversely, that the movement of the center of mass is relatively small

for a given change in slope when the slope is great. (The sine of the angle, which is the function used for plotting, is very nearly in direct proportion to the absolute value of the angle for the small angles investigated. The sine was used in plotting because of the fact that the component of the force of gravity parallel with the slope of the table, and

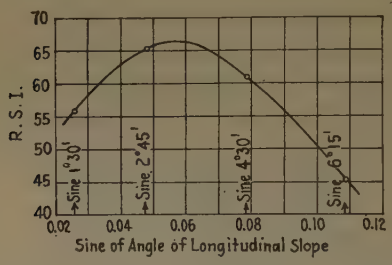


FIG. 36.—R. S. I.—LONGITUDINAL SLOPE.

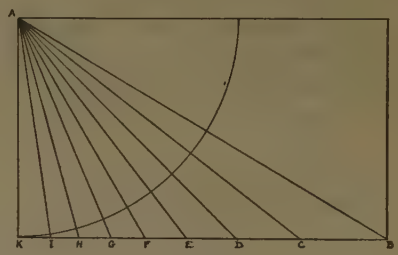


FIG. 37.

therefore effective to move the particles down slope, is proportional to the sine of the angle of inclination.) It is possible that this interpretation of the curves is right in part, but there is a simple geometrical explanation to account for the shape of the curve. In Fig. 37, if $AB$

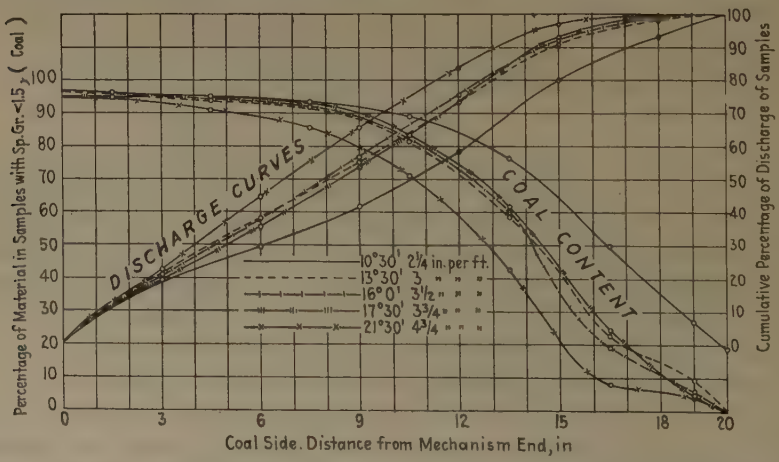


FIG. 38.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERING TRANSVERSE SLOPE.

represents the path of a particle with, say, zero longitudinal slope, and $AC$, $AD$, . . . $AI$ represent paths departing from $AB$ by successive equal angular increments around $A$, then it will be seen that even if equal angular increments in longitudinal slope of the table deck produce equal though different angular increments in the departure of the successive lines of travel from the line $AB$ (which would indicate a straight-line relation between angle of longitudinal slope and angular direction of

travel of particles), yet, because direction of travel is measured by the position of the intersections of these direction lines with the table edge *BK*, the displacements of the lines of travel along this edge will be great for small slopes and small for large slopes, which is precisely the condition indicated in Fig. 35. The authors are inclined to the belief that this is the true explanation for a large part of the curvature shown.

Maximum spread between mean coal and mean slate discharge curves in Fig. 35 occurs somewhere in the neighborhood of ⅝ in. per ft., which will be seen by reference to Fig. 36 to be the slope for optimum operation.

### General Observations on Changes in Longitudinal Slope

This adjustment shows the least effect on efficiency of any so far investigated and, with the exception of change in transverse slope, the least of all. The change in efficiency per inch of movement of the point of discharge of the center of mass of the table bed is the least found with any of the adjustments (see Table 19), which indicates that while change in longitudinal slope affects to a large extent the direction of travel of the bed as a whole, it has little effect on the stratification or on the direction of travel of individual layers in the bed.

### Effect of Variation in Transverse Slope

Lateral slope was investigated over a range of 2¼ to 4¾ in. per ft. with the other variables held constant at the following values: air quantity, 375 cu. ft. per min.; stroke length, ½ in.; 390 strokes per min.; longitudinal slope, ⅝ in. per ft.; rocker-arm angle, 17½°. The feed rate was about 4000 g. per minute.

The experimental results are summarized in Tables 13 and 14, and derived values for the run in Table 15.

The discharge curves on Fig. 38 are rather closely bunched, showing that within the range of adjustment investigated there was but little effect on discharge. All three intermediate rates show fairly even distribution of material on the table deck. The run at minimum slope (2¼ in. per ft.) caused some material to be discharged from the slate end, but with all other slopes a complete and fairly uniform discharge along the coal side only was obtained. The curves for the three intermediate slopes are bunched nearest the straight line from origin to the natural converging point of these curves. For these operations the last 10 per cent. is discharged in the last 6 to 7 in. of the coal side and contains a maximum of 50 per cent. coal, sloping thereafter very rapidly with an inflection point at about 20 per cent. coal content. The desirability of this type of coal-content curve was pointed out on page 175. Analysis of Figs. 39 to 43 inclusive, by the methods already developed, shows a tendency, with minimum slope, to crowd the discharge of large coal, bone and slate near the slate end. Figs. 40, 41 and 42 are closely

TABLE 13.—*Specific-gravity Analyses of Table Discharges with Different Transverse Slopes*

[For Explanation of Letters, see Table 1]

| Angle of lateral slope... | 10° 30′ | 13° 30′ | 16° 0′ | 17° 30′ | 21° 30′ |
|---|---|---|---|---|---|
| Weight of sample, g.... | 1000 | 1000 | 1000 | 1000 | 1000 |
| Calculated percentage of feed +1.5 sp. gr... | 20.61 | 21.35 | 19.84 | 19.26 | 21.83 |
| Position of center of mass of discharge in inches from feed end.. | 9.83 | 8.98 | 8.02 | 8.27 | 7.11 |

| Sample Mark | Sp. Gr. Classification | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_1$ | $F$ | 185.1 | 178.3 | 96.3 | 215.2 | 206.3 | 95.8 | 206.2 | 197.7 | 95.8 | 191.9 | 182.2 | 95.0 | 220.0 | 208.2 | 94.6 |
| | $S_1$ | | 2.7 | | | 3.0 | | | 2.1 | | | 4.2 | | | 4.9 | |
| | $S_2$ | | 4.1 | | | 5.9 | | | 6.4 | | | 5.5 | | | 6.9 | |
| $X_2$ | $F$ | 106.7 | 101.4 | 95.0 | 167.4 | 156.5 | 93.5 | 173.5 | 163.1 | 94.0 | 165.2 | 155.3 | 94.0 | 226.0 | 205.7 | 91.0 |
| | $S_1$ | | 5.3 | | | 10.9 | | | 10.4 | | | 9.9 | | | 20.3 | |
| | $S_2$ | | | | | | | | | | | | | | | |
| $X_3$ | $F$ | 125.9 | 117.5 | 93.4 | 168.2 | 153.8 | 91.4 | 184.2 | 168.9 | 91.7 | 177.1 | 165.0 | 93.2 | 209.0 | 178.3 | 85.3 |
| | $S_1$ | | 5.0 | | | 8.9 | | | 7.2 | | | 6.9 | | | 18.1 | |
| | $S_2$ | | 3.4 | | | 5.5 | | | 8.1 | | | 5.2 | | | 12.6 | |
| $X_4$ | $F$ | 168.9 | 150.3 | 89.0 | 179.5 | 145.4 | 81.0 | 194.2 | 159.3 | 82.0 | 200.7 | 167.7 | 83.5 | 184.3 | 130.9 | 71.0 |
| | $S_1$ | | 18.6 | | | 34.1 | | | 34.9 | | | 33.0 | | | 53.4 | |
| | $S_2$ | | | | | | | | | | | | | | | |
| $X_5$ | $F$ | 217.2 | 165.7 | 76.3 | 181.0 | 106.6 | 58.8 | 165.6 | 99.4 | 60.0 | 197.2 | 122.1 | 61.9 | 132.4 | 56.4 | 42.7 |
| | $S_1$ | | 29.5 | | | 26.1 | | | 19.6 | | | 21.7 | | | 10.5 | |
| | $S_2$ | | 22.0 | | | 48.3 | | | 46.6 | | | 53.4 | | | 65.5 | |
| $X_6$ | $F$ | 129.3 | 64.6 | 49.9 | 71.2 | 16.2 | 22.8 | 64.9 | 12.5 | 19.2 | 60.4 | 14.7 | 24.4 | 26.0 | 2.1 | 8.1 |
| | $S_1$ | | 17.9 | | | 5.7 | | | 0.8 | | | 2.8 | | | 0.4 | |
| | $S_2$ | | 46.8 | | | 49.3 | | | 51.6 | | | 42.9 | | | 23.5 | |
| $X_7$ | $F$ | 41.5 | 11.2 | 27.0 | 17.5 | 1.7 | 9.7 | 11.4 | 0.7 | 6.1 | 7.5 | 0.4 | 5.3 | 2.3 | 0.1 | 4.3 |
| | $S_1$ | | 2.8 | | | 0.1 | | | | | | 0.2 | | | | |
| | $S_2$ | | 27.5 | | | 15.7 | | | 10.7 | | | 6.9 | | | 2.2 | |
| $X_8$ | $F$ | 25.4 | 4.9 | 19.3 | ←Discharge over end of table | | | | | | | | | | | |
| | $S_1$ | | 0.8 | | | | | | | | | | | | | |
| | $S_2$ | | 19.7 | | | | | | | | | | | | | |

TABLE 14.—*Sizing Analyses of Table Discharges with Different Transverse Slopes*

[For Explanation of Letters, see Table 1]

| Angle of lateral slope.. | | 10° 30′ | | | 13° 30′ | | | 16° 0′ | | | 17° 30′ | | | 21° 30′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight of Sp. Gr.-Size Groups in Grams | | | | | | | | | | | | | | |
| Size Groups | | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ |
| $X_1$ | $F$ | 35.5 | 123.3 | 19.5 | 55.7 | 129.7 | 20.9 | 55.5 | 116.2 | 26.0 | 51.2 | 112.0 | 19.0 | 72.3 | 112.2 | 23.7 |
| | $S_1$ | 0.6 | 1.5 | 0.6 | 1.7 | 1.0 | 0.3 | 0.6 | 1.0 | 0.5 | 1.7 | 1.6 | 0.9 | 2.9 | 1.7 | 0.3 |
| | $S_2$ | 0.7 | 1.7 | 1.7 | 1.0 | 2.2 | 2.7 | 1.4 | 1.6 | 3.4 | 1.2 | 2.2 | 2.1 | 2.5 | 2.3 | 2.1 |
| $X_2$ | $F$ | 29.0 | 67.9 | 4.5 | 65.0 | 86.5 | 5.0 | 64.0 | 89.1 | 10.0 | 65.0 | 86.3 | 4.0 | 91.7 | 100.0 | 14.0 |
| | $S_1$ | 2.0 | | * | 3.5 | | * | 3.5 | | * | 2.5 | | * | 10.0 | | * |
| | $S_2$ | 0.8 | 1.7 | | 1.5 | 1.5 | | 2.4 | 1.6 | | 1.3 | 2.4 | | 3.2 | 2.7 | |
| $X_3$ | $F$ | 58.2 | 57.1 | 2.2 | 88.5 | 61.8 | 3.5 | 90.7 | 73.2 | 5.0 | 106.4 | 55.5 | 3.1 | 95.4 | 78.7 | 4.2 |
| | $S_1$ | 4.1 | 0.8 | 0.1 | 7.0 | 1.6 | 0.3 | 6.2 | 0.9 | 0.1 | 5.1 | 1.7 | 0.1 | 16.2 | 1.7 | 0.2 |
| | $S_2$ | 1.0 | 1.8 | 0.6 | 3.3 | 1.5 | 0.7 | 4.0 | 2.9 | 1.2 | 1.5 | 2.6 | 1.1 | 6.0 | 5.3 | 1.3 |
| $X_4$ | $F$ | 96.0 | 52.3 | 2.0 | 101.0 | 42.0 | 2.4 | 105.8 | 51.5 | 2.0 | 130.0 | 35.7 | 2.0 | 80.9 | 48.0 | 2.0 |
| | $S_1$ | 11.0 | | * | 16.5 | | * | 17.5 | | * | 18.0 | | * | 15.0 | | * |
| | $S_2$ | 3.0 | 4.0 | | 12.0 | 4.5 | | 7.0 | 8.0 | | 7.5 | 4.0 | | 27.5 | 10.5 | |
| $X_5$ | $F$ | 115.2 | 49.0 | 1.5 | 74.2 | 31.2 | 1.2 | 67.2 | 31.3 | 0.9 | 94.5 | 26.6 | 1.0 | 38.0 | 17.6 | 0.8 |
| | $S_1$ | 27.9 | 1.5 | 0.1 | 24.1 | 1.9 | 0.1 | 18.0 | 1.4 | 0.2 | 20.2 | 1.4 | 0.1 | 8.6 | 1.6 | 0.3 |
| | $S_2$ | 10.9 | 10.0 | 1.1 | 34.0 | 11.6 | 2.7 | 30.5 | 14.8 | 1.3 | 36.8 | 13.9 | 2.7 | 44.8 | 18.7 | 2.0 |
| $X_6$ | $F$ | 47.2 | 16.7 | 0.7 | 8.8 | 6.9 | 0.5 | 7.0 | 5.1 | 0.4 | 9.9 | 4.6 | 0.2 | 1.2 | 0.8 | 0.1 |
| | $S_1$ | 17.1 | 0.7 | 0.1 | 4.9 | 0.7 | 0.1 | 0.4 | 0.4 | | 2.4 | 0.4 | | 0.3 | 0.1 | |
| | $S_2$ | 33.1 | 12.3 | 1.4 | 35.8 | 12.1 | 1.4 | 37.7 | 12.6 | 1.3 | 33.2 | 8.8 | 0.9 | 14.5 | 10.1 | 0.9 |
| $X_7$ | $F$ | 6.9 | 4.0 | 0.3 | 0.6 | 1.0 | 0.1 | 0.2 | 0.5 | | 0.2 | 0.2 | | 0.1 | | |
| | $S_1$ | 2.3 | 0.5 | | | 0.1 | | | | | 0.2 | | | | | |
| | $S_2$ | 19.6 | 7.0 | 0.9 | 10.6 | 4.6 | 0.5 | 7.6 | 2.8 | 0.3 | 5.3 | 1.4 | 0.2 | 1.2 | 0.9 | 0.1 |
| $X^8$ | $F$ | 1.9 | 2.7 | 0.3 | ←Discharge over end of table | | | | | | | | | | | |
| | $S_1$ | 0.6 | 0.2 | | | | | | | | | | | | | |
| | $S_2$ | 11.4 | 7.5 | 0.8 | | | | | | | | | | | | |

* These figures are calculated from graphs.

TABLE 15.—*Calculations for R. S. I.; Transverse Slope the Variable*

| Lateral slope, deg. | 10° 30′ | 13° 30′ | 16° 0′ | 17° 30′ | 21° 30′ |
|---|---|---|---|---|---|
| Lateral slope, in. per ft | 2.22 | 2.88 | 3.44 | 3.79 | 4.73 |
| Total impurity in sample of 1000 g | 206.1 | 213.5 | 198.4 | 192.6 | 218.3 |
| Impurity in coal, g | 61.5 | 60.0 | 55.6 | 56.0 | 72.7 |
| Impurity in middling, g | 72.1 | 75.9 | 66.5 | 66.1 | 72.1 |
| Impurity in slate, g | 72.5 | 77.6 | 76.3 | 70.5 | 73.5 |
| Middling impurity allotted to coal, g | 33.1 | 33.1 | 28.0 | 29.2 | 35.8 |
| Middling impurity allotted to slate, g | 39.0 | 42.8 | 38.5 | 36.9 | 36.3 |
| Adjusted impurity in coal, g | 94.6 | 93.1 | 83.6 | 85.2 | 108.5 |
| Adjusted impurity in slate, g | 111.5 | 120.4 | 114.8 | 107.4 | 109.8 |
| R. S. I. | 54.1 | 56.4 | 57.8 | 55.8 | 50.3 |

similar and have all of the characteristics indicative of good operation. Fig. 43 shows crowding toward the mechanism end and little separation of bone from coarse coal.

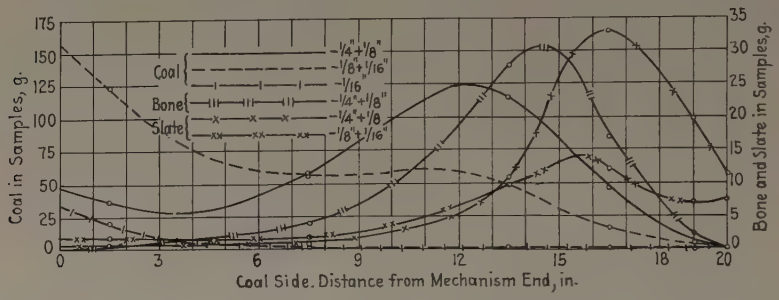


FIG. 39.—POSITION OF DISCHARGE WITH LATERAL SLOPE EQUAL TO 10° 30′.

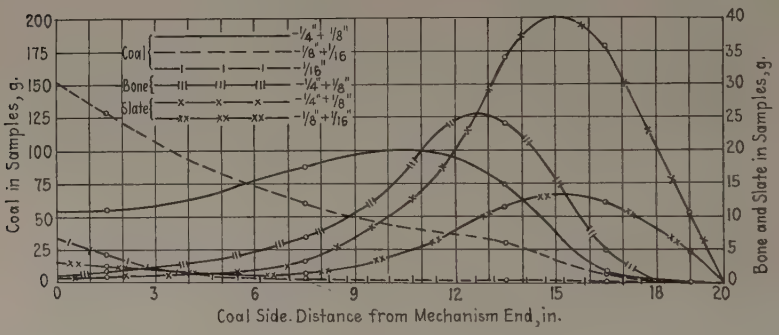


FIG. 40.—POSITION OF DISCHARGE WITH LATERAL SLOPE EQUAL TO 13° 30′.

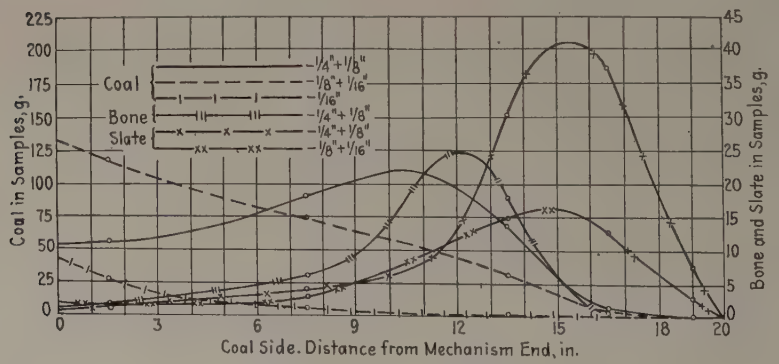


FIG. 41.—POSITION OF DISCHARGE WITH LATERAL SLOPE EQUAL TO 16° 0′.

Fig. 45 shows substantially straight-line relation between the angle of transverse slope and the position of discharge on the table edge for all of the individual products and therefore, also, of the table bed as a

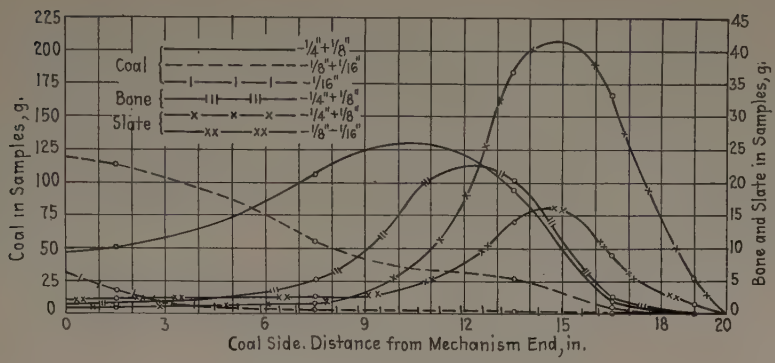


FIG. 42.—POSITION OF DISCHARGE WITH LATERAL SLOPE EQUAL TO 17° 30′.

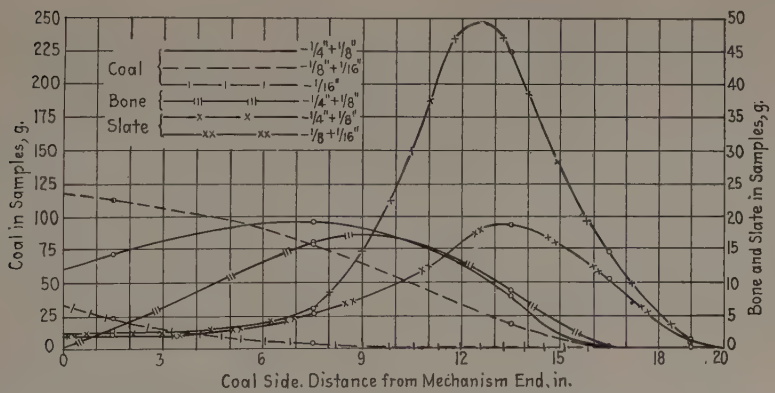


FIG. 43.—POSITION OF DISCHARGE WITH LATERAL SLOPE EQUAL TO 21° 30′.

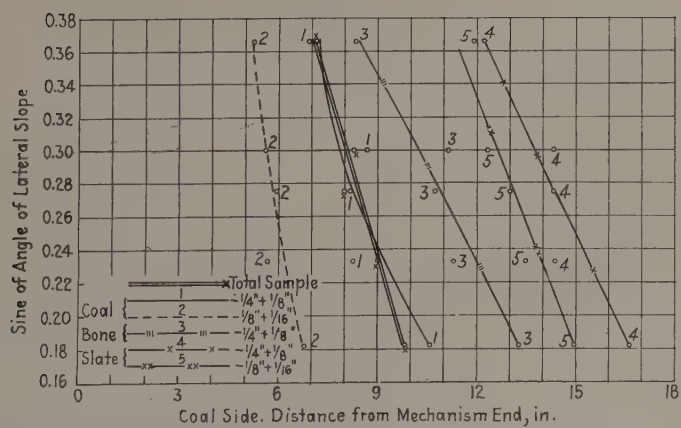


FIG. 44.—RELATION BETWEEN POSITIONS OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND TRANSVERSE SLOPE.

whole. Maximum spread between coal and slate occurs with minimum slope. The flat efficiency curve explains the disagreement between this indication and that of the discharge curves of Fig. 38, showing that transverse slope may be varied over a considerable range without any serious change in results. From this it would seem safe to conclude further that with any given size of feed, transverse slope might well be fixed in table construction; certainly no expensive or intricate provisions for varying this adjustment are justified.

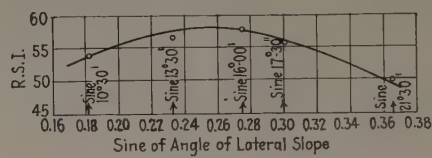


FIG. 45.—R. S. I.—LATERAL SLOPE.

## General Observations on Transverse Slope

Table 19 shows that change in transverse slope through a range of more than 100 per cent. of a workable minimum (2¼ to 4¾ in. per ft.) produces only 2½ in. travel of the discharge point of the center of mass parallel to the table axis and has the least effect on efficiency of any of the other adjustments tested. Figs. 39 to 43, inclusive, show that this adjustment has almost no effect on stratification. Taken together these facts mean that given sufficient fluidity to effect satisfactory stratification, a slope of 2¼ in. per ft. is nearly sufficient to produce proper flow down slope, while the riffling holds back the bed enough, even with 4¾-in. slope, to prevent bunching the discharge at the mechanism end to a great enough extent to destroy separation.

## Effect of Changes in Rocker-arm Angle

In this series of tests the rocker-arm angle was varied from 9° to 27½° with the vertical, while the other variables were held constant as follows: air, 375 cu. ft. per min.; length of stroke, ½ in.; speed, 390 strokes per min.; longitudinal slope, ⅝ in. per ft.; transverse slope, 3½ in. per ft. The feed rate was about 3400 g. per minute.

The experimental results are tabulated in Tables 16 and 17 and the derived data in Table 18.

The discharge curves in Fig. 46 show a wide difference in character of distribution of the material on the table deck. The optimum condition, judged from uniformity of distribution of the discharge, occurs at or near an angle of 22° 30′, and this is confirmed by Fig. 53.

Fig. 47 indicates, by the position and direction of the coal curves, that coarse coal was on top. The crowding toward the mechanism end shows

TABLE 16.—*Specific-gravity Analyses of Table Discharges with Rocker-arms Set at Different Angles from the Vertical*

[For Explanation of Letters, see Table 1]

| Rocker-arm angle | | 9° 0′ | | | 13° 0′ | | | 17° 30′ | | | 22° 30′ | | | 27° 30′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight of sample, g | | 1000 | | | 1000 | | | 1000 | | | 1000 | | | 1000 | | |
| Calculated percentage of feed +1.5 sp. gr. | | 16.28 | | | 17.76 | | | 19.84 | | | 18.52 | | | 18.24 | | |
| Position of center of mass of discharge in inches from feed end. | | 2.95 | | | 4.32 | | | 8.02 | | | 10.24 | | | 13.38 | | |
| Sample Mark | Sp. Gr. Classification | Total Weight of Samples, | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages. | Total Weight of Samples, G. | Partial Weights, G. | Percentages | Total Weight of Samples, G. | Partial Weights, G. | Percentages |
| $X_1$ | $F$ | 645.0 | 576.4 | 89.4 | 508.0 | 470.6 | 92.6 | 206.2 | 197.7 | 95.8 | 117.4 | 113.1 | 96.3 | 34.7 | 33.3 | 96.0 |
| | $S_1$ | | 34.3 | | | 24.7 | | | 2.1 | | | 1.0 | | | 0.2 | |
| | $S_2$ | | 34.3 | | | 12.7 | | | 6.4 | | | 3.3 | | | 1.2 | |
| $X_2$ | $F$ | 255.4 | 204.2 | 80.0 | 230.1 | 202.6 | 88.0 | 173.5 | 163.1 | 94.0 | 98.0 | 93.9 | 95.8 | 29.9 | 28.8 | 96.2 |
| | $S_1$ | | 51.2 | | | 27.5 | | | 10.4 | | | 4.1 | | | 1.1 | |
| | $S_2$ | | | | | | | | | | | | | | | |
| $X_3$ | $F$ | 74.9 | 48.2 | 64.3 | 132.5 | 102.4 | 77.3 | 184.2 | 168.9 | 91.7 | 148.9 | 141.9 | 95.3 | 74.6 | 72.0 | 96.5 |
| | $S_1$ | | 3.4 | | | 12.7 | | | 7.2 | | | 3.8 | | | 1.0 | |
| | $S_2$ | | 23.3 | | | 17.4 | | | 8.1 | | | 3.2 | | | 1.6 | |
| $X_4$ | $F$ | 20.4 | 7.5 | 36.8 | 79.2 | 38.8 | 49.0 | 194.2 | 159.3 | 82.0 | 209.0 | 194.5 | 93.0 | 159.6 | 152.4 | 95.5 |
| | $S_1$ | | 0.2 | | | 40.4 | | | 34.9 | | | 14.5 | | | 7.2 | |
| | $S_2$ | | 12.7 | | | | | | | | | | | | | |
| $X_5$ | $F$ | 4.3 | 0.9 | 20.9 | 44.1 | 7.8 | 17.7 | 165.6 | 99.4 | 60.0 | 264.0 | 211.4 | 80.2 | 316.5 | 297.0 | 93.8 |
| | $S_1$ | | | | | 1.4 | | | 19.6 | | | 25.6 | | | 10.4 | |
| | $S_2$ | | 3.4 | | | 34.9 | | | 46.6 | | | 27.0 | | | 9.1 | |
| $X_6$ | $F$ | No discharge so far | | | 6.1 | 0.2 | 3.3 | 64.9 | 12.5 | 19.2 | 130.6 | 56.9 | 43.6 | 255.6 | 185.8 | 72.7 |
| | $S_1$ | | | | | | | | 0.8 | | | 13.7 | | | 35.8 | |
| | $S_2$ | | | | | 5.9 | | | 51.6 | | | 60.0 | | | 34.0 | |
| $X_7$ | $F$ | | | | | | | 11.4 | 0.7 | 6.1 | 32.1 | 3.1 | 9.7 | 101.0 | 42.7 | 42.3 |
| | $S_1$ | | | | | | | | | | | 0.2 | | | 8.7 | |
| | $S_2$ | | | | | | | | 10.7 | | | 28.8 | | | 49.6 | |
| $X_8$ | $F$ | Discharge over end of table→ | | | | | | | | | | | | 28.1 | 5.6 | 19.9 |
| | $S_1$ | | | | | | | | | | | | | | 0.8 | |
| | $S_2$ | | | | | | | | | | | | | | 21.7 | |

TABLE 17.—*Sizing Analyses of Table Discharges with Rocker-arms Set at Different Angles from the Vertical*

[For Explanation of Letters, see Table 1]

| Rocker-arm angle | | 9° 0′ | | | 13° 0′ | | | 17° 30′ | | | 22° 30′ | | | 27° 30′ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Weight of Sp. Gr.-Size Groups in Grams | | | | | | | | | | | | | | |
| Size Groups | | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ | −¼″ +⅛″ | −⅛″ +1/16″ | −1/16″ |
| $X_1$ | $F$ | 328.2 | 224.0 | 24.2 | 184.0 | 246.1 | 40.5 | 55.5 | 116.2 | 26.0 | 12.1 | 85.5 | 15.5 | 0.2 | 18.0 | 15.1 |
| | $S_1$ | 29.7 | 4.2 | 0.4 | 22.7 | 1.7 | 0.3 | 0.6 | 1.0 | 0.5 | 0.3 | 0.6 | 0.1 | | 0.1 | 0.1 |
| | $S_2$ | 16.3 | 13.2 | 4.8 | 1.1 | 6.5 | 5.1 | 1.4 | 1.6 | 3.4 | 0.7 | 1.4 | 1.2 | | 0.2 | 1.0 |
| $X_2$ | $F$ | 118.5 | 78.5 | | 115.0 | 75.0 | 12.6 | 64.0 | 89.1 | 10.0 | 25.0 | 63.9 | 5.0 | 1.0 | 20.8 | 7.0 |
| | $S_1$ | 13.0 | | * | 16.0 | | * | 3.5 | | * | 0.4 | | * | | | * |
| | $S_2$ | 19.5 | 7.5 | | 5.0 | 5.0 | | 2.4 | 1.6 | | 0.7 | 1.4 | | | 0.3 | |
| $X_3$ | $F$ | 32.0 | 15.7 | 0.5 | 66.3 | 34.8 | 1.3 | 90.7 | 73.2 | 5.0 | 69.7 | 69.8 | 2.4 | 7.8 | 58.4 | 5.8 |
| | $S_1$ | 3.2 | 0.2 | | 11.2 | 1.4 | 0.1 | 6.2 | 0.9 | 0.1 | 2.6 | 1.0 | 0.2 | 0.3 | 0.6 | 0.1 |
| | $S_2$ | 19.4 | 3.4 | 0.5 | 10.2 | 6.1 | 1.1 | 4.0 | 2.9 | 1.2 | 0.7 | 1.8 | 0.7 | 0.1 | 0.7 | 0.8 |
| $X_4$ | $F$ | 3.6 | 3.7 | 0.2 | 23.0 | 15.0 | 0.8 | 105.8 | 51.5 | 2.0 | 122.7 | 70.0 | 1.8 | 63.7 | 84.7 | 4.0 |
| | $S_1$ | | 0.2 | | 5.5 | | * | 17.5 | | * | 8.3 | | * | 2.0 | | * |
| | $S_2$ | 10.2 | 2.2 | 0.3 | 21.0 | 10.5 | | 7.0 | 8.0 | | 2.0 | 2.5 | | 1.5 | 1.7 | |
| $X_5$ | $F$ | | 0.7 | 0.2 | 4.2 | 3.3 | 0.3 | 67.2 | 31.3 | 0.9 | 141.8 | 68.4 | 1.2 | 203.2 | 91.3 | 2.5 |
| | $S_1$ | | | | 1.3 | 0.1 | | 18.0 | 1.4 | 0.2 | 24.8 | 0.8 | | 9.0 | 1.2 | 0.2 |
| | $S_2$ | 2.5 | 0.8 | 0.1 | 25.5 | 8.6 | 0.8 | 30.5 | 14.8 | 1.3 | 16.8 | 9.0 | 1.2 | 4.3 | 3.7 | 1.1 |
| $X_6$ | $F$ | | | | 0.2 | | | 7.0 | 5.1 | 0.4 | 40.8 | 15.5 | 0.6 | 130.2 | 54.2 | 1.4 |
| | $S_1$ | | | | | | | 0.4 | 0.4 | | 12.9 | 0.7 | 0.1 | 33.8 | 1.6 | 0.4 |
| | $S_2$ | | | | 4.0 | 1.8 | 0.1 | 37.7 | 12.6 | 1.3 | 42.9 | 16.0 | 1.1 | 24.5 | 7.9 | 1.6 |
| $X_7$ | $F$ | | | | | | | 0.2 | 0.5 | | 1.7 | 1.3 | 0.1 | 28.5 | 13.6 | 0.6 |
| | $S_1$ | | | | | | | | | | 0.1 | 0.1 | | 8.2 | 0.5 | |
| | $S_2$ | | | | | | | 7.6 | 2.8 | 0.3 | 20.6 | 7.5 | 0.7 | 37.2 | 11.0 | 1.4 |
| $X_8$ | $F$ | Discharge over end of table → | | | | | | | | | | | | 2.5 | 2.9 | 0.2 |
| | $S_1$ | | | | | | | | | | | | | 0.7 | 0.1 | |
| | $S_2$ | | | | | | | | | | | | | 13.9 | 7.1 | 0.7 |

* These figures are calculated from graphs.

TABLE 18.—*Calculations for R. S. I.; Rocker-arm Angle the Variable*

| Rocker-arm angle | 9° 0′ | 13° 0′ | 17° 30′ | 22° 30′ | 27° 30′ |
|---|---|---|---|---|---|
| Total impurity in sample of 1000 g | 162.8 | 177.6 | 198.4 | 185.2 | 182.4 |
| Impurity in coal, g | 76.9 | 59.3 | 55.6 | 48.0 | 46.7 |
| Impurity in middling, g | 42.9 | 46.9 | 66.5 | 62.3 | 68.4 |
| Impurity in slate, g | 43.0 | 71.4 | 76.3 | 74.9 | 67.3 |
| Middling impurity allotted to coal, g | 27.5 | 21.3 | 28.0 | 24.4 | 28.0 |
| Middling impurity allotted to slate, g | 15.4 | 25.6 | 38.5 | 37.9 | 40.4 |
| Adjusted impurity in coal, g | 104.4 | 80.6 | 83.6 | 72.4 | 74.7 |
| Adjusted impurity in slate, g | 58.4 | 97.0 | 114.8 | 112.8 | 107.7 |
| R. S. I. | 35.8 | 54.6 | 57.8 | 60.9 | 50.9 |

TABLE 19.—*Effect of Change in Transverse Slope on Range of Discharge Point and on Efficiency*

| Series | Range in Efficiency, Per Cent. | Range of Discharge Point of Center of Mass, In. | Change in Percentage Efficiency per In. Change in Position of Discharge of Center of Mass |
|---|---|---|---|
| Air | 50 | 7½ | 6.7 |
| Length of stroke | 40 | 6 | 6.7 |
| Speed | 43 | 10½ | 4.1 |
| Longitudinal slope | 22 | 12 | 1.8 |
| Transverse slope | 7½ | 2½ | 3.0 |
| Rocker-arm angle | 26 | 10 | 2.6 |

that the inclination of the initial trajectory of the particles from the horizontal was insufficient to cause effective forward travel of the bed. Fig. 48 shows a much better condition with intermediate coal at the top of the bed. The coal and bone curves on this sheet are of a distinctly desirable nature, *i. e.*, with a gradual downward slope to the right, and the slate curves also are of distinctly improved shape as compared to those

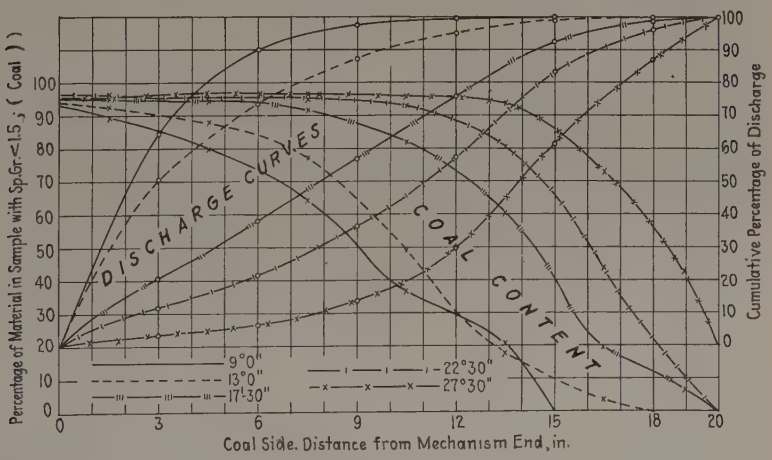


FIG. 46.—RATES AND ANALYSES OF TABLE DISCHARGES WITH DIFFERENT ROCKER-ARM ANGLES.

in the preceding figure, although the slopes of the sides of these slate curves are not yet sufficiently steep to indicate optimum performance, and the fine-slate curve shows too much of this matter discharging in the first few inches from the mechanism end. Fig. 49 shows what appears to be a close approach to ideal conditions, the only objectionable feature being the relatively high quantity of slate discharged at and near the mechanism end. Fig. 50, which is for a rocker-arm angle that

corresponds to the maximum point in the efficiency curve (Fig. 53), shows less slate near the mechanism end than any of the preceding

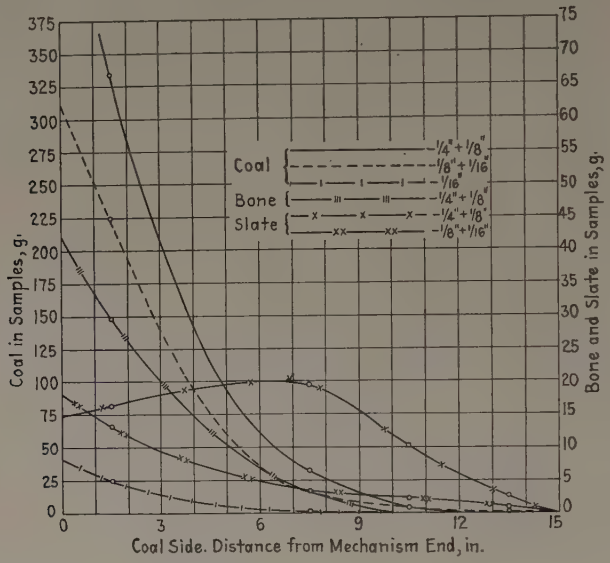


FIG. 47.—POSITION OF DISCHARGE WITH ROCKER-ARM ANGLE EQUAL TO 9° 0′.

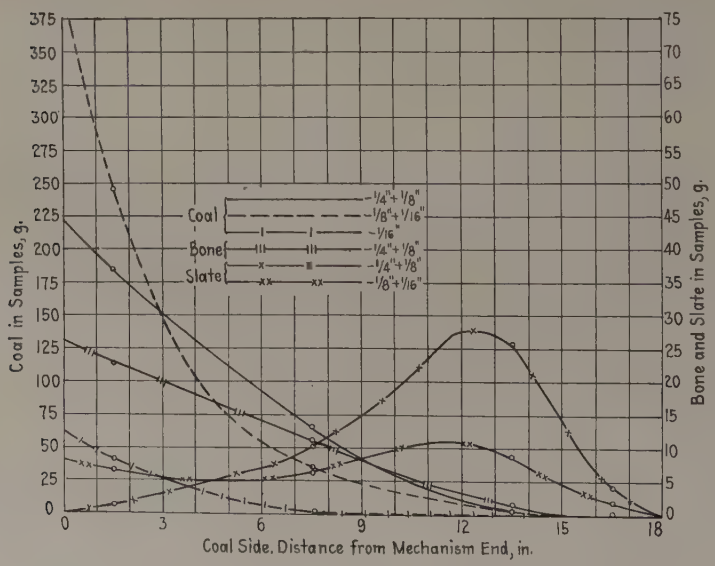


FIG. 48.—POSITION OF DISCHARGE WITH ROCKER-ARM ANGLE EQUAL TO 13° 0′.

figures, the slate and coal peaks are far enough apart to afford practical operating conditions, the bone is fairly central of the valley between the

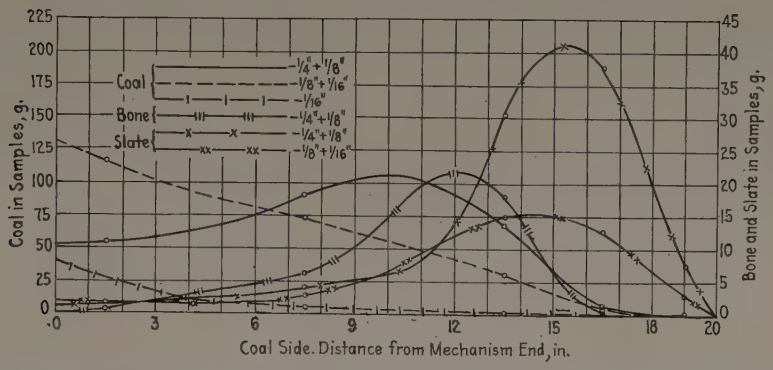


FIG. 49.—POSITION OF DISCHARGE WITH ROCKER-ARM ANGLE EQUAL TO 17° 30′.

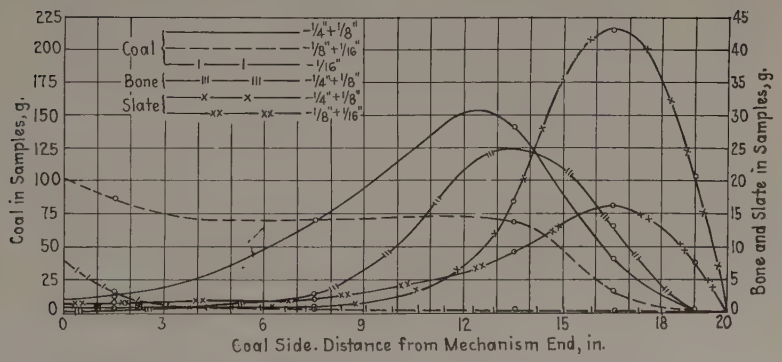


FIG. 50.—POSITION OF DISCHARGE WITH ROCKER-ARM ANGLE EQUAL TO 22° 30′.

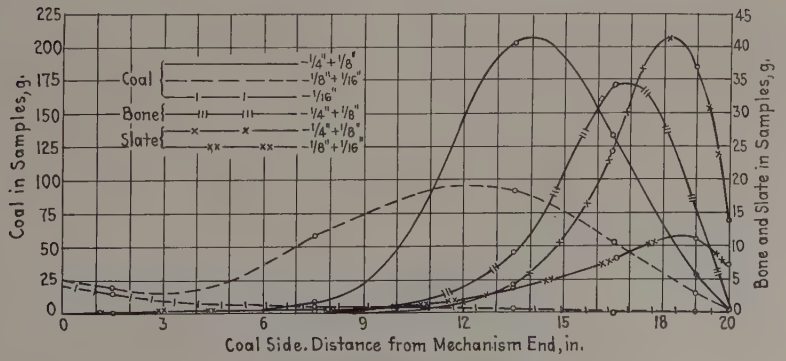


FIG. 51.—POSITION OF DISCHARGE WITH ROCKER-ARM ANGLE EQUAL TO 27° 30′.

peaks for coal and slate, and the slopes of the coal and slate peaks are reasonably steep. Fig. 51 shows the whole separation crowded too far toward the slate end.

Fig. 52 shows an approximation to straight-line variation between the sine of twice the rocker-arm angle and the position of discharge of the

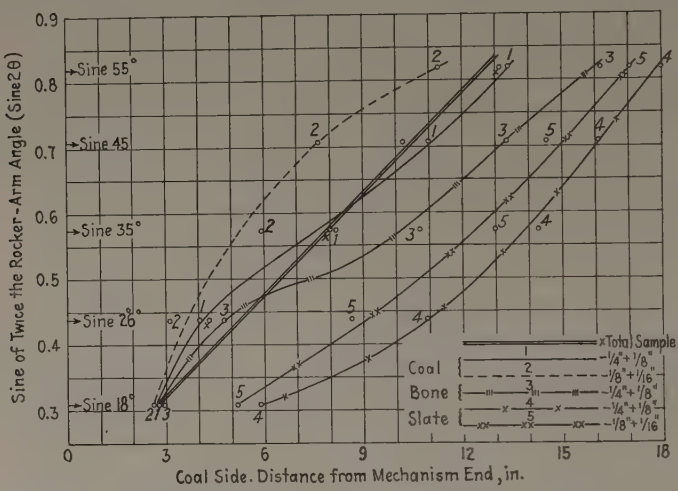


FIG. 52.—RELATION BETWEEN POSITION OF DISCHARGE OF CENTERS OF MASS OF VARIOUS CONSTITUENTS OF BED AND ROCKER-ARM ANGLE.

center of mass of the various products along the table bed. The maximum spread between mean coal and mean slate discharges comes near the point corresponding to a rocker-arm angle of 22° 30′, and the point of optimum operation thus placed corresponds to the point indicated by the other methods of estimation.

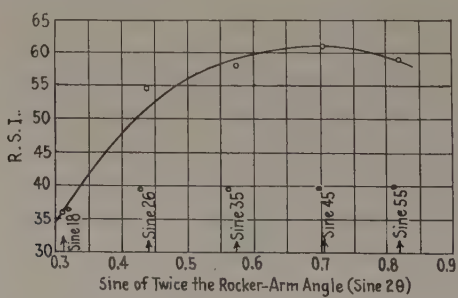


FIG. 53.—R. S. I.—ROCKER-ARM ANGLE.

The sine of twice the rocker-arm angle was chosen as the scale of abscissas for the reason that this is one of the factors in the product determining the horizontal travel of a projectile. (See p 184). The substantial approximation of the curves to a straight line is confirmation

of the conclusion previously stated, that the travel along the deck is in accord with this law.

### General Observations on Rocker-arm Angle

This adjustment, together with those of speed and stroke length, determines the length of the trajectory of particles parallel to the deck axis, and the three are dependent determinants of the rate of forward travel of the bed. Longitudinal slope is an independent determinant of the same movement. But the three dependent adjustments also affect, together with the air supply, the stratification of the bed, which is not affected by transverse slope. Hence the order of adjustment should be, first, to effect a balance between air supply and the dependent three that will give proper stratification, bearing in mind that steep rocker-arm slope and high speed with relatively small air supply may produce the same result as their converse and more economically; then to distribute the discharge uniformly along the deck edge by variation in longitudinal slope.

### Photographic Study of Movement of Particles on Table Deck

Fig. 54 shows a series of snapshots (1/100 sec. exposure) taken through the glass side of a modified table top. The modified arrangement comprised a new deck with the same nainsook base as before, but the riffles were removed and a 1½-in. strip along the center of the table, parallel to the direction of shaking, was enclosed between parallel pieces of plate glass about 3 in. high, fastened to the deck frame so as to make a tight joint with the surface of the nainsook. A glass-sided, open-ended channel was thus formed. The rest of the table deck was covered with a fine-mesh punched plate to hold down the nainsook and also prevent excessive discharge of air through the parts of the deck unoccupied by a bed. With this arrangement it was possible to observe through the glass a longitudinal section on the bed under conditions which are, in so far as it is possible to judge, entirely similar to those existing on a table in regular operation. The upright hinged pin in the upper left-hand corner of the photographs oscillates freely between two stops on the mounting plate, which is attached to the glass wall of the observation compartment. The inertia of the pin tends to hold it stationary with respect to the earth, with the result that, since its support is moving, the inclination of the line joining its center with the center of support is a measure of the position of the support with respect to the central position of the pin. The pointer projecting down into the field near the center of the photographs is fixed in position on the frame. The white dot near the pointer is on the moving glass side. When the dot is at the left of the pointer the table deck is in some one of the series of positions assumed in passing from the center of the backward stroke to

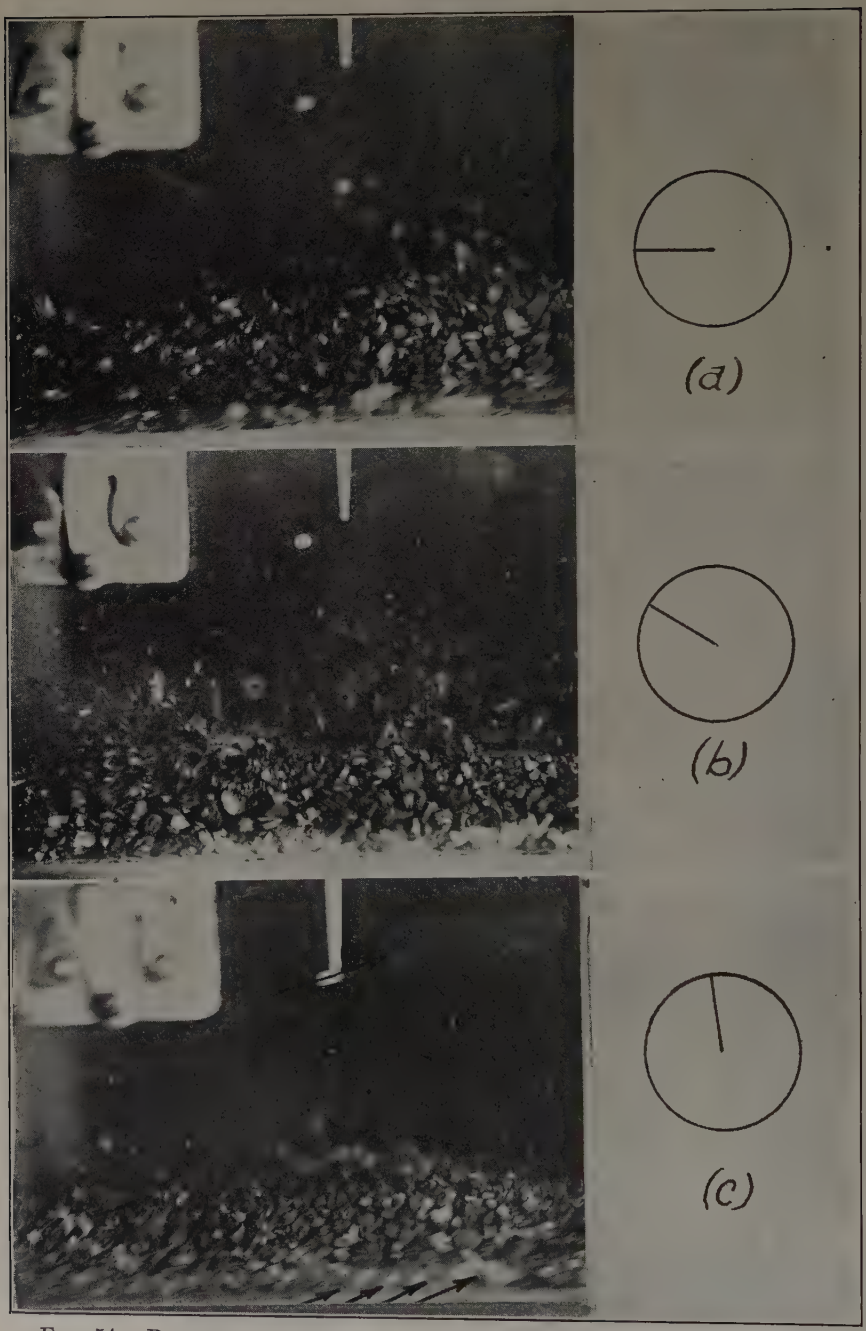


FIG. 54.—PHOTOGRAPHIC STUDY OF MOVEMENT OF PARTICLES ON TABLE DECK.

*a*, Deck is at back of stroke; *b* to *i*, inclusive, positions between *a* and a point slightly more than halfway on backward stroke.

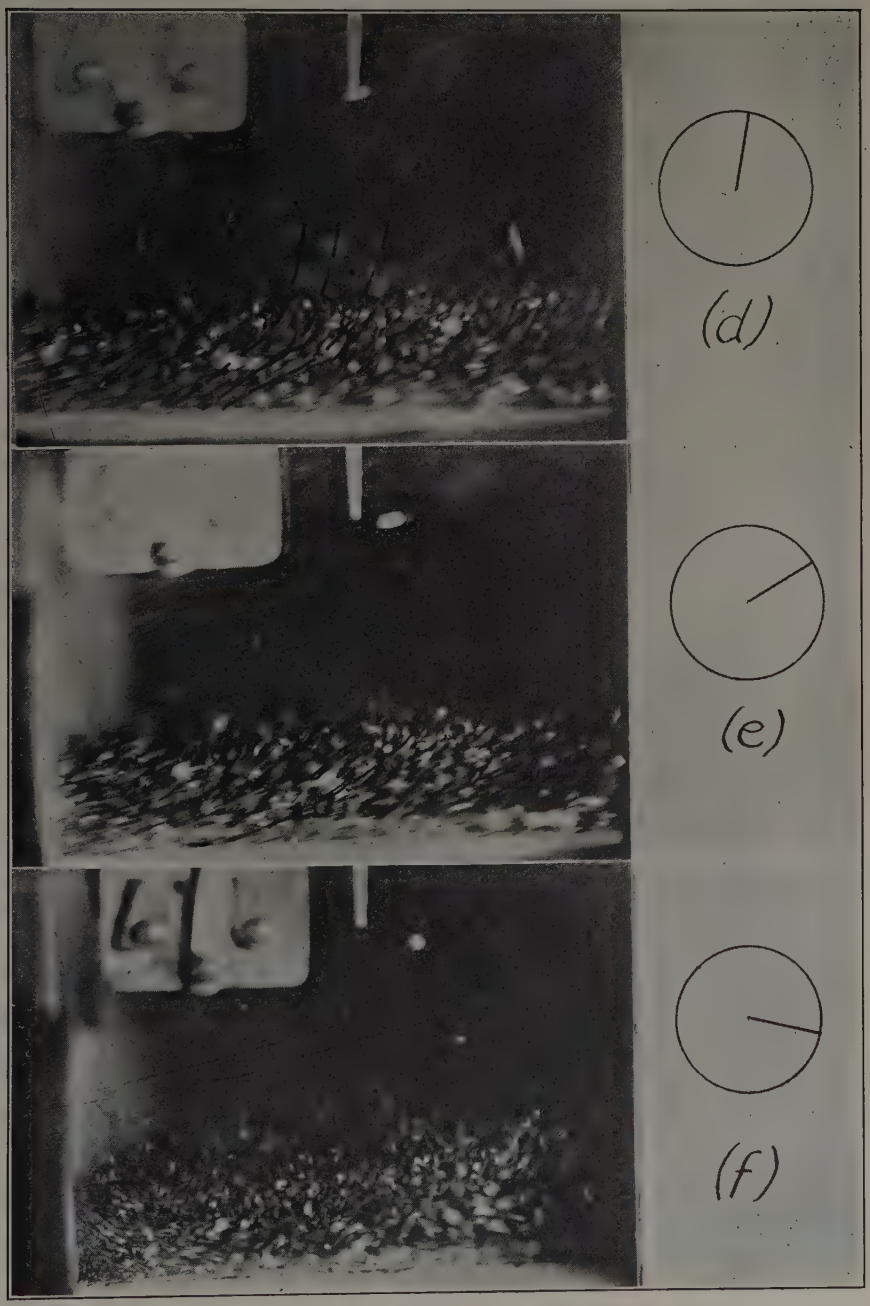


FIG. 54.—(*Continued*).

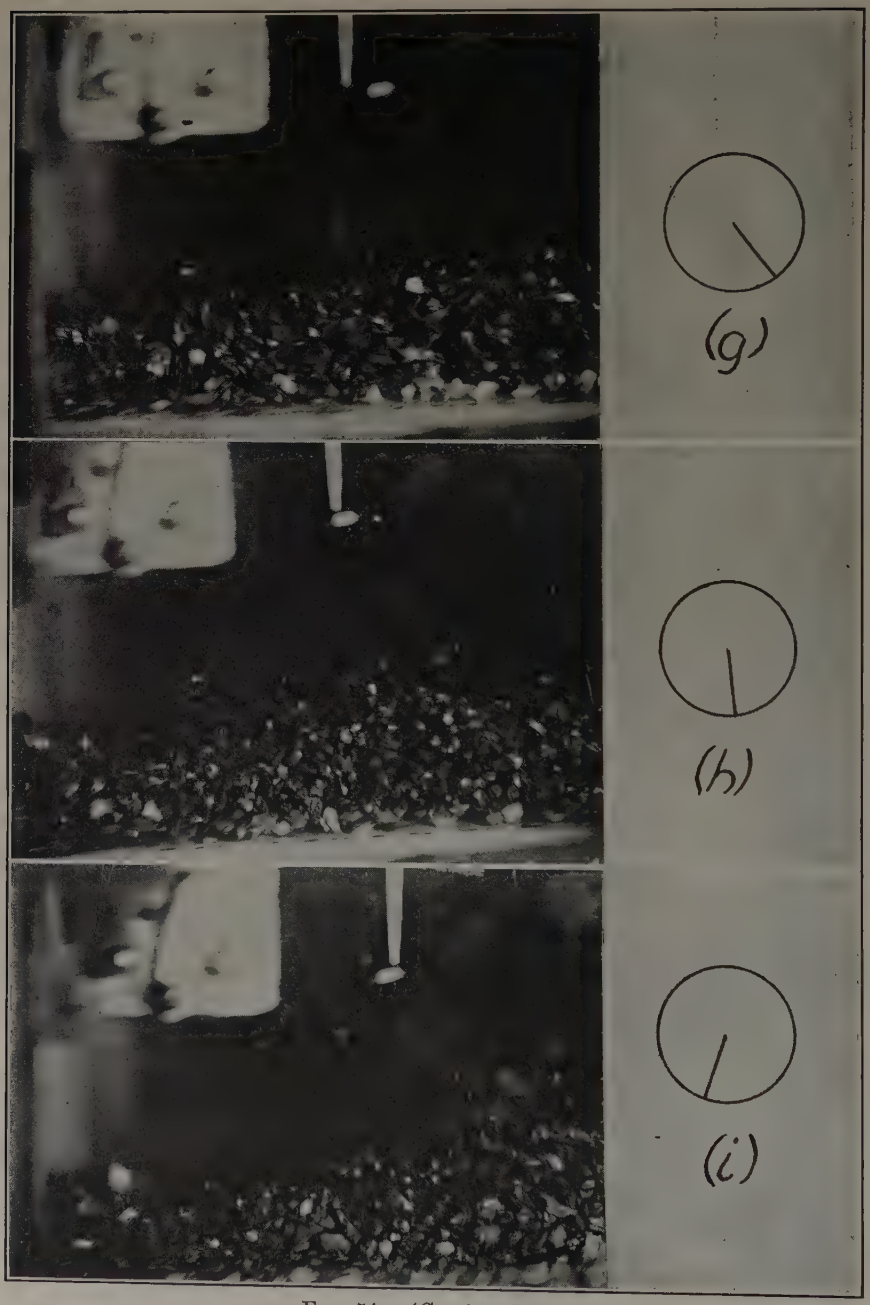


FIG. 54.—(*Continued*).

the center of the forward stroke. The relative position of the table deck at the time any one of the series of photographs was taken can be read from the position of the inertia pointer and the relation of the fixed pointer and dot, and is indicated by the position of the radius in the circle drawn just below the photograph. Thus in Fig. 54*a* the position finders indicate that the deck was at the back end of the stroke, just starting forward. Figs. 54*b* to *i*, inclusive, constitute a series showing a succession of positions between this and a point slightly more than halfway on the backward stroke.

The series of photographs, all having been taken with the camera at rest, indicate by the sharpness of the images the velocities relative to the camera of the objects photographed; by the color, white quartz and black bituminous coal are to be distinguished; while by the direction of the axes of the blurred images, the lines of motion of the particles are shown. The direction of motion along these lines can only be inferred from the position data, so far as the authors are now able to interpret the photographs.

Fig. 54*b* shows the main position of the bed substantially at rest; in *c* the lower stratum was in rapid motion to the right and upward, as indicated by the arrows which interpret the blurs, while the upper stratum was just beginning to move; in *d* the whole bed was in rapid motion, but the curvature of the blurs indicating the paths of the particles, accented by the guide lines drawn on the photograph, shows persistence of the retardation of the upper layer which was commented on in discussing the preceding photograph. Fig. 54*e* indicates somewhat slower motion than was present when the preceding photograph was taken, and slightly greater compacting of the bed, both of which facts demonstrate that the mass was nearing a comparative rest position at the forward end of the stroke. In *f* the whole bed is in confusion at the point of reversal. Figs. 54*g* to *i*, inclusive, indicate that a comparative rest condition obtained in all but the lowest stratum throughout the backstroke.

In Fig. 54*g* the comparative sharpness of image of the lowest stratum indicates that these particles have already come to rest while those in the upper strata are yet moving forward. In 54*h* the table has progressed somewhat farther on its return path and the upper strata are more distinct than the corresponding strata in *g* or the lower stratum in *h*. Fig. 54*i* shows the lower stratum moving rapidly as compared to the upper, and this figure, although resembling *c* closely, shows the blurred lower stratum composed apparently of overturning or tumbling particles rather than of particles traveling in parallel lines like those in *c*. The interpretation of the appearance of Fig. 54*i* is that the lower stratum is being drawn backward under much more slowly traveling upper strata.

The left-hand margin of the photographs is, in all cases, the beginning of the deck at the mechanism end. Fig. 54*b* shows that in about one-third the length of the photograph (about 1 in. actual distance) the white quartz particles have become segregated at the bottom of the

*a*

*b*

Fig. 55.—Effect of air quantity on stratification with respect to size. *a*, Insufficient air supply; *b*, excessive air supply.

bed and that considerable size segregation of coal with intermediate and fine at the top has also taken place within the same distance.

Comparison of Figs. 54*a* to *d*, inclusive, with Figs. 54*f* to *h*, inclusive, shows an apparently thicker bed in the last three. Closer inspection shows that the last three are less closely packed than the first four. These two facts taken together mean that the bed is temporarily unsup-

ported in the second group of photographs and that the particles are settling against the force of the rising air currents, while in the first group the bed is compacted by the rising deck underneath it. It is during the time that the particles are in this suspended and fluid condition that segregation and stratification occur.

Fig. 55 shows the effect of air quantity on stratification with respect to size. With insufficient air supply (Fig. 55*a*) the coarse material collects at the top and the fine at the bottom of the bed. The other extreme is brought out by Fig. 55*b*. Here, because of a slightly excessive quantity of air, the finest material is in temporary suspension above the mass of the bed. The optimum condition lies between these two but distinctly toward that pictured in Fig. 55*b*.

The projectile-like motion of the particles parallel to the deck axis is well illustrated by Figs. 54*c* to *f*, inclusive. In *c*, as previously noted, the lower particles are moving to the right and upward. The angle that their direction makes with the horizontal is greater than that of the deck motion itself at this point (note the angle between the arrows indicating respectively the directions of deck and particle motions), which shows that the particles are out of contact with the deck and traveling in the direction of the impulse imparted earlier in the stroke while the rocker arms were inclined further from the vertical. In *d* the direction of the lowest stratum is still about the same as in *c*. The motion of the upper strata is more nearly vertical, due partly to a lag of these strata and partly to the greater effect on the lighter particles of the substantially vertical air currents. In *e* the direction of the lowest stratum is nearly horizontal—the top of the trajectory—and the horizontal component of motion of the upper part of the bed has increased. The blurs at the right in *f* are distinctly to the right and downward; these particles are on the downward leg of the trajectory and nearing the end of their flight.

The sequence of motions thus read was confirmed by visual inspection, both of the bed that was photographed and of individual larger particles.

## Summary

From the foregoing experiments, the action of a crude coal undergoing separation on the deck of a pneumatic table may be summarized.

As soon as the stream of feed comes into contact with the table deck it begins to move parallel to the axis under the influence of the shaking motion and the push of other material behind it. The motion of the deck exerts a force on the particles, the magnitude and direction of which are determined by the three adjustments, length of stroke, number of strokes per minute and rocker-arm angle. The effect of the applied force is to throw the particles forward and upward out of contact with the deck surface, to which they quickly settle again. In settling

they are opposed by a force due to the upward motion of air forced through the porous deck covering. If the force of the air is insufficient to impede the fall effectively, the particles stratify according to difference in size alone; the large particles interlock and bridge as they begin to compact, leaving voids between them into which the smaller particles penetrate. After a few repetitions of this cycle a segregation is effected with the coarse particles at the top and the fine at the bottom of the mass, but in neither the fine nor the coarse stratum is there any effective segregation of particles of different specific gravities.

If the rising current of air has sufficient velocity, the force that it exerts will be enough to cause a difference in settling rates of particles between particles of the same size and different specific gravities, the heavier, of course, settling the more rapidly. Then, after a few repetitions of the shaking cycle, the lowest stratum will be composed principally of coarse slate; above and in contact with this, a layer of coarse bone, and above this, in turn a layer of coarse coal. With the correct quantity of air and a feed sized within proper limits, the finer coal will be unable to penetrate the bed of coarse particles to any sensible extent, and will form a layer on top; fine bone and slate will, on the other hand, penetrate the bone into and toward the bottom of the coarse coal layer and down into the upper part of the coarse bone layer, the slate to the bottom of the coarse bone and down a certain distance into the coarse slate.

It is possible to consider stratification from another viewpoint, *viz.:* that suspension of the solids in the rising air current forms a mixture of air and solids that has the effect of a heavy fluid, similar to that used in the Chance process, in which the heavy slate sinks but on which the light coal floats. This is, however, so far as our present knowledge goes, pure hypothesis, since we have no independent evidence for this particular fluid property of the bed mixture.

Shape, unfortunately, is a factor in stratification. Coal, for the most part, breaks into roughly cubical lumps; slate and bone are normally decidedly flaky. Thus a flat piece of the heavier material of a given weight may present a greater surface to the rising air than a piece of coal of the same weight and be correspondingly retarded in its fall. This relative retardation increases as the flakiness becomes more pronounced, with the result that considerable impurity of this flaky variety is invariably found in the coal strata and, consequently, in the cleaned coal.

By the time that stratification is complete the particular batch of crude coal under consideration will have progressed a short distance away from the feed point and its components will then be subject to the forces that will determine the position of their discharge along the deck periphery. These forces may be classified into two groups, acting substantially at right angles to each other, one group parallel to the axis of the table, the other transversely to this axis in the plane of the deck.

The first group consists of two forces: (1) the propulsive force of the deck motion, previously analyzed, and (2) a component of the force of gravity parallel to the deck surface, due to the longitudinal slope of the deck and directed, usually, toward the mechanism (feed) end of the deck, therefore opposing the other force of the group.

The other group consists likewise of two forces: (1) a component of the force of gravity, directed toward the coal-discharge side of the deck and due to the transverse slope, and (2) a component of the supporting force of the riffle cleats opposing the first member of the group.

If the air supply and deck motion are properly adjusted to effect stratification, the bed is sufficiently fluid and mobile to flow down the transverse slope readily. But transverse flow of the lower strata is positively prevented by the riffle cleats so that the strata lying below the tops of these cleats are constrained to a resultant path parallel to the axis of the table, if the propulsive force of the deck motion is sufficient to force the bed up the longitudinal slope. The upper strata, not being constrained, follow a diagonal path that is the resultant of the resultant longitudinal force and the transverse component of gravity, and reach the discharge edge at a point that depends upon the relative magnitudes of these two forces, *i. e.*, upon the steepness of the transverse and longitudinal slopes and upon the shaking-motion adjustment. As the bedded material in the riffle grooves moves forward, the vertical taper of the riffle cleats removes the transverse support from successively lower strata and these, in turn, follow their diagonal path toward the discharge edge, but starting this diagonal as they do after they have been constrained to travel some distance toward the slate end, their point of discharge is nearer the slate end than that of the original top strata. By suitable splitters arranged along the discharge periphery actual physical separation into the grades originally segregated vertically in the bed on the table may be effected.

It will be noted the air supply was not included in the foregoing discussion as one of the adjustments that influenced the direction of travel on the table deck. The omission was due to the fact that the air does not, except accidentally, exert a force having a component in the plane of the deck. But in its effect on fluidity of the bed the air supply has an enormous effect on the position of discharge, particularly of the upper (coal) layers of the bed. Air supply is, as a matter of fact, the most potent adjustment in the operation of a pneumatic table and should be made readily and accurately controllable, where this is not already the case. It should, however, be impressed on operators that any increase in air supply above that necessary to effect proper stratification is to gain the desired fluidity in the most expensive way, since the same effect can usually be obtained by increasing the number of mechanical impulses per unit of time and directing them more nearly vertically

upward, in other words, by increasing the number of strokes per minute (decreasing stroke length, if necessary) and increasing the angularity of the rocker arms. The experiments set forth in this paper, although performed on a finer feed than normally prevails in practice, indicate that higher table speeds, shorter strokes, and greater rocker-arm angularity than are used in any of the plants visited by the writers, would well repay trial in some, if not all, of the plants visited.

Pneumatic-table practice has suffered, ever since its inception, from the effects of the assumption that the action on the table deck is the same as or closely similar to that on the deck of wet shaking tables. But the two operations differ in several essential particulars. In the first place the size stratification on a wet table is, in so far as the lighter material is concerned, exactly the reverse of that on a pneumatic table, while there is no size segregation of the heavy material. There is some stratification according to the specific gravities of the feed constituents but, owing to the size stratification of the light material, fine light material is intermingled with the fine and coarse heavy material at the bottom of the bed. These facts are due to the almost complete lack of a rising current of fluid in the bed and to the further fact that the motion of the deck is in or almost in the plane of the deck.

In the second place, transverse travel on a wet table is due almost entirely to the force exerted by the flow of feed and wash water transversely. This force is subject to ready control through a wide range, both by adjustment of the quantity of water and by the transverse slope, and it is a force whose magnitude is greater than any of the directional forces on a pneumatic table. Hence transverse tilt and wash-water supply are the adjustments most used in wet-table operation, and the practice has been carried over, in so far as is possible, to the pneumatic plants, in the form of an adjustment of transverse tilt. But Fig. 44, compared with the corresponding summaries of the effects of the other adjustments, shows that this adjustment is the least potent of all in its effect both on the direction of flow and the efficiency of operation.

Cross-water is depended upon, by reason of its sizing action,[1] to overcome the lack of definite stratification in the bed, and complete the separation after the material has emerged from the riffles onto the plane section of the deck. There is no such supplementary concentrating action available on the pneumatic table.

These are the principal points of difference between the two tables, but they are sufficient to demand of the pneumatic-table operator complete divorce from wet-table practice, if he would hope for the best, or even for satisfactory operation of his dry tables.

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[1] A. F. Taggart: Handbook of Ore Dressing. New York, 1927. John Wiley & Sons.

# DISCUSSION

E. O'Toole, Gary, W. Va. (written discussion).—This paper is indeed worthy of commendation. Its 60 pages of concentrated data—descriptive, tabular, graphic and photographic—undoubtedly represent many long hours of serious painstaking effort along lines of research which are of no little importance today and are ever becoming more important with the steady increase in the commercial treatment of coal by the pneumatic process.

The prime worth of this paper, however, lies in the method of portraying and analyzing the results of the individual tests rather than in the numerical values of the findings. The authors have shown an accurate analysis of the problem confronting them and have in all cases attacked its solution in a thorough and logical manner. Among other items their Relative Separation Index particularly appeals to me. If not original with them, it is at least new to me, and offers a convenient means of equalizing the results of tests conducted under differing conditions of product proportioning, with or without recirculating middlings, and should prove a handy tool for others working along the same lines. My customary procedure in such work has been to make the product cuts conform as nearly as possible by visual inspection with the desired specific gravity of separation and then to compute both qualitative and quantitative efficiencies. The product of these two is then considered as the general efficiency, which thereby properly penalizes whichever phase of the separation has been favored by the possibly incorrect product proportioning and correspondingly rewards the opposite phase to which the cutting has been disadvantageous. Thus errors in setting the cutting fingers are practically eliminated in the computation of the efficiencies. When, however, actual complete weights of products are used in compiling results of such tests, the cleaned coal and refuse matter remaining upon the deck at the completion of the test run, as well as any unreturned middlings, must be deducted from the crude feed or distributed in some more or less arbitrary manner between the clean coal and refuse, in order to obtain test result figures which are truly representative. In general, I should say that the R. S. I. used by the authors of this paper will serve practically the same purpose as this general efficiency computation, with considerably less labor involved.

It is unfortunate, however, that these tests were not performed on a standard commercial unit, or at least on a model more nearly approaching it, as in that event the resultant findings might have been more nearly applicable to practical operation. From the authors' description, the deck used by them resembles the older types used for treating seeds, nuts, cereals, etc., more nearly than it does the modern coal-treating units—and the distance between the two is considerable! Although the pneumatic process was successfully applied to the treatment of coal in 1921, practical commercial operation on an economic basis really dates from the first use of the so-called Y-deck in 1925.

There have been, in fact, but three noteworthy developments in the art of pneumatic separation during the past eight years. The first of these was the introduction of a direct obstruction in the path of the refuse in order to form a "banking zone." This made possible the carrying of a heavier bed on the deck without clean coal being mechanically carried over with the refuse. This in turn made possible tonnages sufficiently high for economical commercial operation and at the same time increased separating efficiency by providing deeper and better stratification. The decks used at this stage still conformed closely to the original types, however, and were restricted to a narrow size range, 2/1 being considered the maximum ratio under average operating conditions.

This disadvantage was eventually overcome by the evolution of the V and Y-type decks, capable of treating far greater size ranges without a corresponding drop in

efficiency. In this type of deck the width decreases as the volume of the bed is diminished by discharging of the clean coal, thus keeping the depth of the bed more nearly uniform and enabling a reasonable thickness of bed to be maintained almost to the extreme end without necessitating an excessive depth at the feed point. The increased length in proportion to the width also produces a zoning action over various portions of the deck surface, independent of the normal stratifying action. This fact enables this type of deck to treat efficiently far wider ranges of sizes than are theoretically possible in accordance with Rittinger's formula or any other accepted computation. Incidentally, this type of deck is not a plane surface but is warped, providing a variation in transverse slopes corresponding to the differences in quality of the materials handled on the different portions of the deck area.

This zoning action has been made more sensitive by the introduction of means for readily controlling the air supply to the different portions of the deck. This is the third great forward step in the pneumatic cleaning of coal, and is in no small degree responsible for the high efficiency and large-range treatment now possible.

It will be readily seen, however, that the several variable factors governing the adjustment of such a unit will not correspond closely with those applicable to a small-scale, old-style deck such as was used by the authors of the paper under discussion. Mr. Lechmere-Oertel is undoubtedly familiar with the laboratory model "Half Y" unit in the Coal Treatment Laboratory of Birmingham University. This unit is only half-size and does not incorporate the latest developments and improvements, and although A. N. Harrison Slade has performed many valuable and interesting experiments upon it, his results do not coincide exactly with actual commercial operating plants in which the standard units are employed. Similar experiments are being conducted by the Fuel Research Board at Greenwich.

The separators with which I am most familiar are those of the American Coal Cleaning Corpn., and most of my premises are necessarily based upon my experience with that equipment. A considerable amount of experiment and research has been conducted at Dallas, Texas, by Messrs. Sutton, Steele & Steele; at Welch, West Virginia, and Ohio State University by the American Coal Cleaning Corpn.; and at Birtley, County Durham, England, by the Birtley Iron Co. In addition, many more trials and tests have been performed in the two score or more commercial plants now utilizing this type of equipment. I am so fortunate as to have access to the reports of these tests.

The normal adjustment of the American separator is based largely on the results of these experiments and an effort has been made to reduce the number of variables to a minimum. Thus the length of stroke has been fixed for all units. Riffle height and spacing as well as deck covering are standardized for the different size ranges in the construction of the deck, which also incorporates fixed transverse slopes suitable for cleaning smaller sizes of coal. For treating the larger sizes, these transverse slopes are made adjustable by means of a central elevating arrangement. Longitudinal slope, reciprocating speed and air supply, both as to total volume and distribution, are adjustable within the limits found necessary to cover the ordinary ranges of operation. The toggle-arm angle is also readily adjustable in the standard machines but it has rarely been found advantageous to alter it from the 60° slope at which it is set in the shop for all standard machines.

In Table 20 are listed the adjustments recorded for the six tests covered by this paper, comparing them with the standard adjustments of the American type Y-54-120 machine, treating ¼ by 0-in. coal of average character.

I have noted with an asterisk the variable factor in each of the tests run and assume from the summary of the paper that test 6 should represent the ideal adjustment. The variation between this and the standard commercial unit is remarkable. For

TABLE 20.—*Adjustments for Six Tests Compared with Standard Adjustments*

| Test No. | Deck Area, Sq. Ft. | Feed, Kg. per Min. | | Air Supply, Cu. Ft. per Min. | | | Stroke | | | Slope (From Horizontal) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Total | Per Sq. Ft. | Total | Per Sq. Ft. | Per Kg. Feed | Length | Frequency | Ft. per Min. | Long. | Transverse | Toggle |
| 1 | 1.495 | 3.2 | 2.14 | *375 | 251 | 117.2 | ½ | 320 | 26⅔ | 2° 45′ | 16° | 72° 30′ |
| 2 | 1.495 | 4.0 | 2.68 | 322 | 215 | 80.5 | *½ | 320 | 26⅔ | 2° 45′ | 16° | 72° 30′ |
| 3 | 1.495 | 3.1 | 2.08 | 322 | 215 | 104.9 | ½ | *390 | 32½ | 2° 45′ | 16° | 72° 30′ |
| 4 | 1.495 | 3.2 | 2.14 | 375 | 251 | 117.2 | ½ | 390 | 32½ | *2° 45′ | 16° | 72° 30′ |
| 5 | 1.495 | 4.0 | 2.68 | 375 | 251 | 93.8 | ½ | 390 | 32½ | 2° 45′ | *16° | 72° 30′ |
| 6 ideal | 1.495 | 3.4 | 2.28 | 375 | 251 | 110.2 | ½ | 390 | 32½ | 2° 45′ | 16° | *67° 30′ |
| Standard Y-54-120 | 32.5 | 377.8 | 11.6 | 4700 | 145 | 12.4 | ⅜ | 340 | 21¼ | 2° 30′ | 4° 45′ | 60° |

* Variable factor.

instance, with an air supply per square foot of deck surface equal to approximately one-half that furnished the test machine, a capacity was obtained equal to five times that of the test unit. At the same time the actual speed of travel of the deck was approximately two-thirds that of the test unit. Roughly assuming the power consumption to be directly proportional to the speed of travel and to the air supply per unit weight of feed, the power consumption of the test machine per unit of capacity is found to be some 12½ times as great as for the commercial machine.

This wide variation is not due solely either to the differences in design or to the small size of the laboratory machine, but at least in part to the fact that practically none of these variables is truly dependent. Practical operation has demonstrated that within reasonable limits the effect of almost any of these variable factors can be overcome by corresponding or inverse changes of other variables. This might seem to indicate the possibility of further reducing the number of these variables, but it must be borne in mind that for each of these omitted, the adjustment of all those remaining is made proportionately sensitive. Referring to the table, however, it will be noted that the ideal air supply was determined during a run in which both the stroke frequency and the toggle or rocker-arm angle were improperly set as compared with the final determination. Similarly the stroke length was determined when air supply, stroke frequency and toggle angle were wrong, and this latter factor was also incorrect when the proper frequency was determined as well as the two slope angles which are judged by the authors to be relatively constant. It is possible that these departures from the supposed ideal in making these various determinations entered in a considerable degree into the numerical results.

Incidentally, it might be well to point out that the slope angles stated for the Y-deck are not true for the entire deck, the surface of which is warped. Thus the longitudinal slope of 2° 30′ represents an end elevation of approximately 2.75° in addition to the built-in slopes, which is about the average condition for this size of coal and produces the indicated angle along the center rib of the deck. This same angle will not be shown in any other longitudinal section. Similarly the 4° 45′ of transverse slope represents the slope of a section taken at the "throat" of the Y. On any section between this and the feed end this angle would be less, while conversely it is increased on all sections between the throat and the refuse end.

Experiments with which I am familiar, covering variations in height, spacing and taper of riffles as well as various step, terrace and undulating arrangements of the riffles, have demonstrated that these factors play a rather prominent part in determining the separating efficiency of pneumatic separators. Changes in deck covering have also a noticeable effect, although not so extensive as that caused by riffle changes.

Distribution of air volumes over various sections of the deck area constitutes an extremely important factor in pneumatic separation and offers a field for extremely valuable and instructive research, and it is to be hoped that in the not too distant future some one will approach this problem in as intelligent and logical a manner as Messrs. Taggart and Lechmere-Oertel have displayed in the presentation of this paper. Furthermore, they have, perhaps unintentionally, made clear a point which is frequently misunderstood in connection with pneumatic separation; they have demonstrated that it is practically a flotation process in which the stratification is governed primarily by the laws governing hindered settling of solid particles in a fluid as contrasted with the frequently expressed opinion that the pneumatic process "blows the clean coal off the table but has not sufficient force to blow the refuse over the riffles." This, of course, is far from the true condition and certain portions of these tests clearly demonstrate this.

# Chemical Reactions in Flotation

By Arthur F. Taggart,* T. C. Taylor† and A. F. Knoll,‡ New York, N. Y.

(New York Meeting, February, 1930)

Some years ago, A. M. Gaudin and one of the authors published a paper showing removal of tar acids from solution by sulfides preferentially as compared to gangues (specifically by galena as compared to quartz).[1]

The underlying phenomenon was classed as adsorption, and the paper went on to develop the general thesis that so far as water-soluble frothing and collecting agents in flotation are concerned, the phenomenon of adsorption is one of controlling importance.

Adsorption was defined in that paper as "a process of rearrangement of a system, which results in establishing a difference in concentration, as between the interfacial layers and the bulk of the phases, of a substance or substances initially uniformly dispersed in one or several of the phases."

The paper went on to develop the relation between adsorption and surface energy according to Gibbs' equation (which may be thrown into the form $U/c = KdT/dc$, where $U$ = excess concentration in surface layer, $c$ = concentration, $T$ = surface tension, and $K$ is a constant), and pointed out that, according to this equation, degree of adsorption and change in surface tension vary directly.

The present paper offers a somewhat different definition for the term adsorption; and sets up, in sweeping terms, the generalization that simple chemical reaction underlies the functioning of the flotation reagents which control mineral collection, when these reagents are soluble in and act from solution in the water of the pulp.

## Adsorption

According to the modified definition, adsorption means concentration at an interface between different phases in a heterogeneous system (thus far the definition runs as before), by the action of some mechanism, of which nothing is properly implied in the word, and concerning which the user of the word is probably in entire ignorance. Thus defined,

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[1] A. F. Taggart and A. M. Gaudin: Surface Tension and Adsorption Phenomena in Flotation. *Trans.* A. I. M. E. (1922) **68**, 479.

adsorption makes sense in probably upwards of 99 per cent. of the places in which it is used in flotation literature.

In the present paper, when the word adsorption stands alone, it is to be read as carrying the meaning of the preceding paragraph.

Experimental work in recent years on the mechanism of the action of flotation reagents in solution leads toward the conclusion that, so far as concentration of those reagents that directly determine collecting is concerned, the mechanism is invariably one of chemical reaction between the reagent and one of the constituents of the ore. When the process is frothing, as distinguished from collection, concentration of the reagent at air-water interfaces may not, so far as our present knowledge goes, be ascribed to chemical reaction in the ordinary sense; and we are forced to fall back, for our statement of mechanism, on the more general basis stated by Gibbs, *viz.:* a reduction in the potential energy, specifically the surface energy, of the system. If this is done with a clear realization of the incompleteness of the picture, there is no harm in it.

## Frothing Agents

It is possible, however, to get a more graphic, though probably no more fundamental picture of the mechanism involved in the action of frothing agents, by considering the distribution of their molecules from the point of view of solubility—more properly, relative solubilities—in the adjacent phases. This is a viewpoint that traces back to Langmuir's articles on the constitution of matter [2] and is developed in full in a recent article by Taggart, Taylor and Ince.[3] According to this conception, a frothing agent is a substance, ordinarily organic, whose molecule may be considered to consist of a water-soluble and a water-insoluble part. Such a molecule is in the position, for it, of maximum stability, when it lies at the interface between air and water, with its water-soluble end toward the water and the other end toward the air. The substance is usually said to be adsorbed at the air-water interface. A form of statement that pretends less and gives more information is that the substance is concentrated at the air-water interface because of the solubility relations of its molecule to the liquid and gaseous phases respectively.

## Collecting Agents

The principal thesis of the present paper is an extension of the conclusion announced in the Taggart, Taylor and Ince paper in the following words: " . . . analysis proves marked removal of collecting agent by the

[2] *Jnl.* Amer. Chem. Soc. (1917) **39,** 1848.
[3] See page 285.

sulfide, and suitable experiment further proves that the material taken out is either the collecting agent as such or in an analogous chemical form readily transformed back to the original compound, or to one closely allied thereto." The extended hypothesis is:

*All dissolved reagents which, in flotation pulps, either by action on the to-be-floated or on the not-to-be-floated particles affect their floatability, function by reason of chemical reactions of well recognized types between the reagent and the particle affected.*

It is intended to embrace within this generalization collecting agents, depressing agents and activating agents, organic and inorganic, subject only to the one limitation that they first dissolve in the water of the pulp; and to exclude frothing agents, agents that react with substances dissolved in the pulp water (protective agents), and agents of whatever kind not in solution. It is not meant by this exclusion to imply that chemical reaction has no part in the functioning of these latter types of substances. Nor the contrary. The exclusion is imposed solely for the purpose of narrowing the discussion to the extent indicated.

No claim is made that the hypothesis set forth is substantiated exhaustively. But this much can be said: There is a considerable amount of reliable evidence for such a conclusion; there is no evidence of similarly conclusive character against, within the knowledge of the authors.

The idea of chemical reaction in flotation is not new. DeBavay[4] suggested that the alkaline carbonates and bicarbonates, which he recommended for use with oils in floating sphalerite, removed carbonates and other impurities from the sphalerite surfaces. The commonly presented explanation for the effectiveness of sulfuric acid in the 10 years 1913–1923, when acid was widely used, was that it dissolved oxide coatings from the sulfides. Solution in both of these cases implies chemical reaction.

Perkins[5] suggested that the action of the organic collecting agents, such as thiocarbanilid, diazo-amino-benzene, thiocresols, xanthates, and the like, was in part chemical.

The early all-aqueous differential-flotation patents[6] aimed to effect, by digestion in strong aqueous solutions, chemical surface changes similar to those effected by the fractional-roasting processes.[7] How thoroughly the surfaces were changed is shown in Fig. 1.

But when some of these same investigators found that very dilute solutions of inorganic substances had somewhat the same effects on the

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[4] De Bavay: U. S. Patent 864597 (1904).

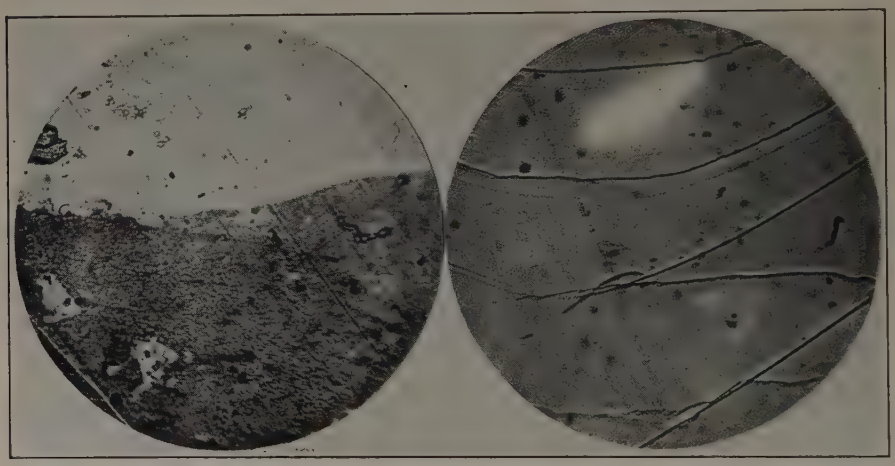
[5] Perkins: U. S. Patent 1364304 (1919).

[6] Ramage, 967671; Wentworth, 970002 and 980035; MacGregor, 972459; Horwood, 1020353; Greenway and Lowry, 1102738; and Lavers, 1142821.

[7] Wentworth, 938732; Ramage, 949002.

floatability of certain sulfides as the strong solutions had, they apparently dropped the chemical-action idea, for the reason that there were, with the dilute solutions, no readily visible surface changes on the minerals affected.

The idea of chemical action in the dilute solutions of modern flotation appears in Stevens patent,[8] for the use of alkali cyanide in the proportions of about one part reagent in 1000 of water. Stevens says that the purpose of the cyanide is to dissolve certain sulfides, which, of course, means chemical action.



(a) (b)

FIG. 1.—GALENA (a) AND SPHALERITE (b), DIGESTED 10 MIN. AT NORMAL TEMPERATURE IN 0.075 PER CENT. SODIUM DICHROMATE SOLUTION. × 185.

None of these various investigators, however, presented any experimental data to confirm his speculation.

Gates and Jacobsen[9] seem to have been the first to publish evidence of chemical reaction between reagent and mineral particle under modern flotation conditions. They worked with sphalerite in copper sulfate solution; and concluded that copper replaces zinc according to the reaction:

$$CuSO_4 + ZnS = ZnSO_4 + CuS$$

Fahrenwald,[10] in a paper amazing in its scope and originality, had already investigated the interaction of copper sulfate on sphalerite (and other sulfides), using changes in hydrogen-ion concentration as indications of interaction, but he unfortunately failed to recognize the true significance of his data and attributed the observed changes in pH to adsorption of ions.

[8] U. S. Patent 1429544, applied for 1920.

[9] *Bull.* 16, Utah Eng. Expt. Sta. (1925).

[10] A. W. Fahrenwald: *Trans.* A. I. M. E. (1924) **70,** 647.

McLachlan[11] reported tests in which quartz, sphalerite, galena, pyrite and pyrrhotite were treated in copper sulfate solution and the residual solution tested for abstraction of copper. Abstraction was shown by all of the sulfides, none by the quartz. The hypothesis was put forth, based on work by Watanabe[12] and Emmons,[13] that CuS was formed on the surface of the sphalerite. It is interesting to note that when chalcopyrite was treated, the residual solution was enriched in copper.

Tucker and Head[14] and Tucker, Gates and Head[15] investigated the visible effects of lime, sodium cyanide and a sodium cyanide-zinc sulfate mixture on the surfaces of various sulfides. They found that there were changes in the sulfide surfaces which were visible under the microscope at relatively low magnifications. These changes, in every case, were greatest on the pyrite and least on the galena. Taggart[16] and Taggart, Taylor and Ince[17] were unable to reproduce the Tucker and Head results. Tucker, Gates and Head report qualitative microchemical tests on material removed from sulfide surfaces coated in the lime-cyanide solution which show definite reactions for iron and lime. The coating from the particle treated with cyanide alone gave a test for ferric iron. These authors suggest that the coatings found when lime is present are calcium carbonate, formed by reaction with carbon dioxide from the air and precipitated preferentially on nuclei formed, in the case of the pyrite at least, by chemical attack on the pyrite by cyanide.

Using the ingenious miniature flotation cell devised by Gates and Jacobsen,[18] Gaudin, Glover, Hansen and Orr,[19] Gaudin and Sorensen,[20] and Gaudin and Martin[21] performed a large number of flotation tests on deslimed pure minerals, both sulfides and non-metallics, with a large variety of organic and inorganic reagents in various combinations. In the papers cited and also in two other papers[22] the results of these tests are discussed and a variety of hypotheses are set forth, some postulating double-decomposition chemical reaction, others "adsorption" in contradistinction to chemical reaction, yet others "adsorption" followed by

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[11] Can. Inst. of Min. and Met. (1926) **19,** 987.

[12] *Econ. Geol.* (1924) **19,** 497.

[13] Emmons: U. S. Geol. Survey, *Bull.* 625, 140.

[14] *Trans.* A. I. M. E. (1926) **73,** 354.

[15] *Idem,* 372.

[16] A. F. Taggart: Handbook of Ore Dressing, 871. New York, 1927. John Wiley & Sons.

[17] *Ante.*

[18] *Ante.*

[19] *Tech. Paper* 1, Utah Eng. Expt. Sta. (1928).

[20] *Tech. Paper* 4, Utah Eng. Expt. Sta. (1928).

[21] *Tech. Paper* 5, Utah Eng. Expt. Sta. (1928).

[22] Flotation Practice, A. I. M. E., (1928) 50. *Eng. & Min. Jnl.* (1927) **124,** 1045.

chemical reaction. Unfortunately, all of these hypotheses are the result of deduction from the flotation tests, with no direct investigation of the phenomena postulated, and the papers present, therefore, no experimental support for the hypothesis of the present paper.[23]

Taylor and Bull[24] and Bull[25] did further work along the lines of that done by the Utah investigators, directed particularly to the effect of cations. They paralleled their flotation tests with measurements of the electrostatic potential of galena particles in various salt solutions, and came to the conclusion that depression of minerals by inorganic salts is due to "adsorption" of the cations of the salt at the mineral surfaces, resulting in a concentration of charges of like sign on the mineral particles, as a result of which charging the particles repel each other and hence, after one particle gets on a bubble, others are prevented from boarding the same bubble. But this theory is built up on the basis of the old and entirely erroneous coursing-bubble theory of mechanism in agitation-froth flotation, and must fall, in its present form, with the explosion of that theory.[26]

Luyken and Bierbrauer[27] investigated the flotation of apatite by sodium palmitate and the reason therefor. They proved, by the Fahrenwald method,[28] that apatite removes sodium palmitate from an aqueous solution, and they postulated that the removal was due to a reaction between the calcium ions of the apatite and the anion of the soap to form relatively insoluble calcium palmitate at the apatite-particle surfaces. On account of analytical difficulties they were unable to check this assumption directly, but they did prove abstraction of sodium palmitate from solution by galena, and on digestion of the coated galena with sulfuric acid recovered palmitate ion far in excess of sodium ion,

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[23] Occasion is regretfully taken here to protest against a form of proof which appears in the work under discussion. At page 12 of the Gaudin and Martin paper (footnote 21), a postulate as to the action of fatty acids on a mixture of calcite and malachite is properly introduced with the words:

"*A possible explanation* for the failure of the fatty acids to act selectively in favor of malachite is as follows: . . . "

At page 36, under the caption "SUMMARY," this same postulate has attained undue and undeserved importance, thus:

"3. The failure of the fatty acids and fatty acid soaps, in the flotation of malachite and azurite from calcite, *has been shown to be due* . . . " (Italics not in the original.)

The material following the quotations is the same at both pages. There is no further evidence on the subject under discussion recorded on the intervening pages.

[24] *Jnl. Phys. Chem.* (1929) **33**, 641.

[25] *Idem*, 656.

[26] See Taggart: *Eng. & Min. Jnl.* (1923) **115**, 113; (1924) **117**, 104 and Handbook of Ore Dressing, 797.

[27] *Mitt.* Kaiser-Wilhelm-Inst. für Eisenforschung (1929) **119**, 37; *Ztsch. tech. phys.* (1929) No. 4, 139.

[28] *Ante.*

and concluded therefrom that the sodium palmitate was not removed by the galena as such and, therefore, that there must have been reaction, resulting in the production of lead palmitate.

These investigators then went on to formulate the further hypothesis that a collecting agent is effective when the compound that it forms with the particle to be floated is less soluble than the unchanged surface of the same particle, and not otherwise. Their experimental evidence for this hypothesis is not convincing, although the hypothesis itself is.

## Action of Collecting Agents

The hypothesis of flotation mechanism set up at page 5 of the present paper, in support of which evidence is herein adduced, may be expanded in detail as follows:

1. The operation of bringing any particle into a condition to float in a froth-flotation operation involves the production at the surface of the particle of a water-repellent coating.[29]

2. Conversely, the operation of depressing any particle involves the maintenance at or production at its surface of a water-avid coating.[30]

3. Production of water-repellent and water-avid surfaces by means of dissolved substances is effected by simple chemical reaction between the reagent and the material of the surface affected.

4. The surface changes are generally of slight extent.

5. When positive collection is the end sought and gained, the surface coating is organic and oriented.

6. Depression may be effected by an oriented or unoriented surface coating, organic or inorganic, or by rendering the particle surface so soluble that no continuing surface is maintained.

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[29] The term water-repellent, as used here, connotes air avidity and indicates something different from insolubility. That is to say: By a water-repellent surface is meant one at which water is readily replaced by air, when air and water are brought simultaneously into contact with it. Solubility in water is sometimes loosely defined, from one point of view, as a preference of the molecules of the substance to surround themselves by water rather than by air. Under such a loose definition, water-repellency and insolubility might be thought to be similar or the same property, in which case an attempt might be made to substitute above the word insoluble for water-repellent. But closer examination of the phenomenon of solution shows that it involves surrounding the molecules (or atoms or ions) of the solute by the molecules of the solvent in preference to the molecules (or atoms or ions) of the solute itself and that the question of preferential contact by the solute with the solvent or with air is in no way involved.

[30] The term water-avid is the converse of water-repellent, but includes the idea of solubility. That is to say: While it is readily conceivable that a water-insoluble surface might be water-avid, it is inconceivable that a water-soluble surface should be water-repellent.

## Solubility and Chemical Interaction of Minerals

The slow rate at which the idea of chemical reaction as the groundwork of flotation phenomena has spread, and the paucity of even present-day knowledge of the details of the reactions involved is probably due to the fact that flotation investigators have been largely ignorant of chemical literature, and chemists of flotation performances. In the early days of flotation, oils were oils: generally neutral inflammable liquids immiscible with water, if the flotation man looked them up in the dictionary; of a variety of physical, technical, chemical and commercial classifications, if he looked a little further; and of bewildering and unplumbed complexity, if he approached them from a purely chemical standpoint. To the chemist seeking light on their behavior in flotation, they exhibited wholly unpredictable and ungeneralizable preferential affinity for metalliferous mineral over gangue, some frothed and some did not, some collected and some did not, some were useful and others were not, some worked with one ore and not with others, and some worked some days on one ore and not on other days on the same ore.

Gradually, however, flotation practice evolved a classification of oils into frothers and collectors, and the independence of the frothing and collecting elements of the flotation process was recognized. Following this recognition, it was discovered that the collecting element could be supplied by definite chemical individuals which dissolved in the water of the pulp. Since an oil coating on the mineral was a known prerequisite to the flotation thereof when oil was used, a similar coating was postulated for the soluble collector and the word adsorption was offered to explain the mechanism involved in producing the postulated coating. Taggart and Gaudin[31] published experimental evidence of the coating but clung to the word adsorption as an explanation thereof.

It is surprising, in view of the literature of geochemistry, that after the discovery of the utility of soluble chemical individuals as collectors, there should not have been almost immediate postulation of chemical reaction as the mechanism of their operation. But, barring the highly tentative feeler of Perkins[32] in 1919, the idea does not begin to appear until 1928. Yet in the Data of Geochemistry,[33] under the chapter heading, "The Decomposition of Rocks," are to be found such statements as follows:

"Rain water falls upon the surface of a rock and sinks more or less deeply into its pores and crevices. Rain . . . carries oxygen and carbon dioxide in solution . . . Water and gas both exert a solvent action, and the fluid which then saturates the rock becomes charged with the products of solution. These may intensify or inhibit

[31] *Ante.*

[32] *Ante.*

[33] F. W. Clarke: *Bull.* 330, U. S. Geol. Survey (1908).

further action, according to circumstances. Some of the dissolved matter, redeposited, may form a protecting film and so delay or prevent further solution."

. . . .

"When meteoric waters act upon a mass of rock, the effects produced will depend upon the nature of the minerals which they encounter . . . pyrite . . . although found in relatively small proportions, is nevertheless important for by oxidation and hydration it yields solutions of sulphate having a distinctly acid reaction. These acid solutions act strongly upon other constituents of rocks, and intensify the activity of the percolating waters."

. . . .

"That nearly all minerals are more or less attacked by water has long been known, and also that carbonated waters act still more energetically . . . Many minerals were tested, and all were perceptibly soluble. From 40 grains of hornblende, digested during forty-eight hours in water charged with carbonic acid, 0.08 grain of silica, 0.095 of ferric oxide, 0.13 of lime and 0.093 of magnesia, or nearly 1 per cent. in all were extracted."

The following data represent further abstracts from the same publication:

. . . .

Orthoclase with pure water yielded $K_2O$, silica and alumina. In water saturated with $CO_2$ there was relatively great solution of silica but relatively less $K_2O$. Leucite was less vigorously attacked than orthoclase. Many minerals are alkaline to litmus when moistened with pure water, *e.g.* several magnesian silicates, augite, amphibole and tremolite; kaolinite, pyrophyllite and nontronite are acid. After digestion of the powdered mineral in carbonated water, adularia lost $SiO_2$, $Al_2O_3$ and $K_2O$; oligoclase, $SiO_2$, $Al_2O_3$, $Na_2O$ and CaO; hornblende, $SiO_2$, CaO and FeO; magnetite, FeO; apatite, CaO and $P_2O_5$; olivine and serpentine, $SiO_2$, MgO and FeO; the amounts in the several cases ranging from 0.3 to upwards of 2 per cent. of the original powder. The question of solubility of the ordinary rock-forming minerals is summarized as follows:

"The evidence, both as found by experiment in the laboratory and by field observations, shows that all minerals, certainly all of the most important ones, are attacked by water and carbonic acid. The pyroxenes and amphiboles yield most readily to waters, then follow the plagioclase feldspars, then orthoclase and the micas, with muscovite the most resistant of all. Even quartz is not quite insoluble. Among the commoner accessories, apatite and pyrite are most easily decomposed, magnetite is less attacked, and such minerals as zircon, corundum, chromite, ilmenite, etc., tend to accumulate with little alteration in the sandy rock residues. These minerals are not absolutely incorrodible, but they are nearly so. Corundum, for example, slowly undergoes hydration, and is converted, at least superficially, into gibbsite or diaspore."

If it be thought that the reactions of geochemistry are not to be read into the flotation machine because geochemical solutions are more concentrated, geochemical temperatures and pressures higher, and the contacts between solutions and particles of infinitely longer duration than in the machine, the following evidence should be considered carefully:

Emmons[34] gives analyses of 41 mine waters. Total salinity ranges from 47 to 237,000 parts per million. Twenty-seven of the waters show

[34] *Ante.*

less than 1000 parts salinity per million. Many of the samples were taken from small bodies of standing water in the mines and were probably more concentrated than typical underground water.

We have found that four parts of distilled water, after five minutes contact with one part of finely powdered ore from the Miami Copper Co., contains about 225 parts dissolved salt per million parts of water. This ore is not unusually decomposed or refractory. Two to four pounds of lime per ton in a 1:1 pulp is not unusual in the ball mill. Such a quantity, all dissolved, would correspond to from 500 to 1000 parts per million of water. McLachlan[35] gave analyses showing 200 to 650 parts dissolved salts per million in the waters from different parts of the Nacozari flotation mill.

Mine waters are surface waters and their temperatures are, therefore, rarely more than a few degrees above normal surface temperatures.

The mean pressures under which ground waters exist are, of course, higher than those in the flotation plant. But operations of heap leaching and leaching in place, as at Ohio Copper Co., have shown that pressure is in no way essential to the dissolving action of the percolating solutions on minerals.

The leaching experiments just cited, as well as the experiments with Miami ore, referred to above, show that long time of contact is not prerequisite to leaching of ore minerals, and no citation is, of course, necessary to establish the fact that once solution is effected, reactions between inorganic substances move quickly toward equilibrium.

Granting, then, that there is possibility or probability, according to your personal bias, of reaction in the flotation machine similar to that which takes place in the rocks, an examination of some of the experimental facts of geochemistry with respect to the reactions of the common ore minerals, as abstracted from Emmons,[36] will be of interest.

Pyrite, of the common sulfides, is the most readily attacked by oxygenated water. The soluble products are ferrous sulfate and sulfuric acid, according to some such equation as the following:

$$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4 \qquad [1]$$

Pyrrhotite reacts similarly and even more readily. Ferrous sulfate oxidizes in the presence of air and oxygen. The products are ferric sulfate and ferric hydroxide. With suitable reservations the following equation may be written for this reaction:

$$6FeSO_4 + 3O + 3H_2O = 2Fe_2(SO_4)_3 + Fe_2(OH)_6 \qquad [2]$$

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[35] Soluble Salts in the Mill Waters of the Nacozari Concentrator and Their Effect on Flotation, Mimeograph, A. I. M. E., February, 1928.

[36] *Ante.*

In the presence of sulfuric acid and oxygen, ferrous sulfate changes to ferric sulfate.

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O \quad [3]$$

is the usual equation set up to represent the reaction. Ferric sulfate hydrolyzes, giving an acid solution and a brown precipitate of ferric hydroxide:

$$Fe_2(SO_4)_3 + 6H_2O = Fe(OH)_3 + 3H_2SO_4 \quad [4]$$

Ferric sulfate attacks the sulfides of copper. Thus

$$Fe_2(SO_4)_3 + Cu_2S = CuSO_4 + 2FeSO_4 + CuS \quad [5]$$

$$Fe_2(SO_4)_3 + CuS + 3O + H_2O = CuSO_4 + 2FeSO_4 + H_2SO_4 \quad [6]$$

Copper sulfate readily attacks all of the common sulfides. The chemistry of this attack is discussed fully by Zies, Allen and Merwin,[37] from whose paper the following equations, experimentally verified, are abstracted:

$$CuS + Cu_2SO_4 = Cu_2S + CuSO_4 \quad [7]$$

$$CuS + 7CuSO_4 + 4H_2O = 4Cu_2S + 4H_2SO_4 \quad [8]$$

$$Cu_2S + CuSO_4 \text{ (qual.)} = Cu + CuSO_4 \text{ (basic)} + H_2SO_4 \quad [9]$$

$$FeS_2 + CuSO_4 \text{ (qual.)} = FeS_2 + CuS + Cu_2S + CuO + Cu + Fe_2O_3 + FeSO_4 + H_2SO_4 \quad [10]$$

$$5FeS_2 + 14CuSO_4 + 12H_2O = 7Cu_2S + 5FeSO_4 + 12H_2SO_4 \quad [11]$$

$$4FeS_2 + 7CuSO_4 + 4H_2O = 7CuS + 4FeSO_4 + 4H_2SO_4 \quad [12]$$

Zies, et al. observed microscopically firmly coherent coatings of both CuS and $Cu_2S$ on pyrite surfaces. They also noted that sulfuric acid slows down reactions 11 and 12 but does not stop them.

Pyrrhotite reacts vigorously with cupric sulfate to form copper sulfides (chalcopyrite, if conditions are right), hematite, metallic copper, cuprite and pyrite as the solid products, and ferrous sulfate, hydrogen sulfide and sulfuric acid in solution [13].

$$5CuFeS_2 + 11CuSO_4 + 8H_2O = 8Cu_2S + 5FeSO_4 + 8H_2SO_4 \quad [14]$$

Cupric sulfide is also formed by this same reaction.

$$Cu_5FeS_4 + CuSO_4 = 2Cu_2S + 2CuS + FeSO_4 \quad [15]$$

$$ZnS + CuSO_4 = CuS + Cu_2S + H_2SO_4 \quad [16]$$

In this reaction cupric sulfide is formed first and cuprous later by the reaction of more cupric sulfate on the cupric sulfide. More cupric sulfide is formed when $H_2SO_4$ is present initially.

$$PbS + CuSO_4 = CuS + PbSO_4 \quad [17]$$

Cupric sulfide goes on to cuprous, in the presence of excess $CuSO_4$, according to equation 8.

Emmons[38] cites an experiment in which pyrite, marcasite, galena, sphalerite and enargite were each separately attacked by leaching with distilled water; and each oxidized to a sulfate, which dissolved. When two of the sulfides were treated together, action on one was greatly accelerated and that on the other retarded. Sphalerite dissolved the more readily in the presence of pyrite. This suggests electrochemical effects, and such an hypothesis finds some support in the following table from Gottschalk and Buehler:[39]

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[37] *Econ. Geol.* (1916) **11,** 408.

[38] *Ante.*

[39] *Econ. Geol.* (1912) **7,** 15.

POTENTIAL IN VOLTS OF SEVERAL SULFIDES, MEASURED IN DISTILLED WATER AGAINST COPPER WIRE

| Mineral | Volts | Mineral | Volts |
|---|---|---|---|
| Marcasite | +0.37 | Chalcocite | +0.14 |
| Argentite | 0.27 | Hematite | 0.08–0.26 |
| Cassiterite | 0.27 | Cuprite | 0.05 |
| Chalcopyrite | 0.18–0.30 | Niccolite | 0.02 |
| Enargite | 0.18–0.23 | Domeykite | 0.01 |
| Molybdenite | 0.20 | Copper metal | 0.00 |
| Covellite | 0.20 | Stibnite | −0.17–0.6 |
| Pyrite | 0.18 | Sphalerite | −0.2 –0.4 |
| Bornite | 0.17 | Zinc metal | −0.83 |
| Galena | 0.15 | | |

These potentials change with the solution, being highest positive in acid and oxidizing solutions and lowest in alkaline and reducing solutions.

$$PbS + 4O = PbSO_4 \qquad [18]$$

$$PbS + Fe_2(SO_4)_3 + H_2O + 3O = PbSO_4 + 2FeSO_4 + H_2SO_4 \qquad [19]$$

Schuerman,[40] on the basis of suitable experiments, has arranged the metals in a series in which the sulfide of any given metal will be precipitated, under sulfide-precipitating conditions, at the expense of any sulfide lower in the series. As a rule the reaction is the more complete the farther apart the metals in the series. The series is:

Pd, Hg, Ag, Cu, Bi, Cd, Sb, Sn, Pb, Zn, Ni, Co, Fe, As, Th, Mn.

Weigel[41] gives the following results of solubility determinations on metallic sulfides:

SOLUBILITY OF SULFIDES OF HEAVY METALS IN DISTILLED WATER AT 18° C. (AFTER WEIGEL)

| Crystalline | Moles per Liter $\times 10^{-6}$ | Mg. per Liter | Freshly Precipitated | Moles per Liter $\times 10^{-6}$ | Mg. per Liter |
|---|---|---|---|---|---|
| MnS | 54.5 | 4.7 | MnS | 71.6 | 6.2 |
| Pyrrhotite | 53.6 | | ZnS | 70.6 | 6.9 |
| Pyrite | 48.9 | 5.9 | FeS | 70.1 | 6.2 |
| Pyrite, artificial | 40.8 | 4.9 | CoS | 41.6 | 3.8 |
| Wurtzite, artificial (ZnS) | 28.8 | 2.8 | NiS | 39.9 | 3.6 |
| Millerite, artificial (NiS) | 16.3 | 1.5 | CdS | 9.0 | 1.3 |
| Greenockite, artificial (CdS) | 9.0 | 1.3 | $Sb_2S_3$ | 5.2 | 1.8 |
| Zincblende | 6.6 | 0.6 | PbS | 3.6 | 0.9 |
| Zincblende, artificial | 6.6 | 0.6 | CuS | 3.5 | 0.3 |
| $Cu_2S$ | 3.1 | 0.5 | $As_2S_3$ | 2.1 | 0.5 |
| Galena | 1.2 | 0.3 | $Ag_2S$ | 0.55 | 0.14 |
| Galena, artificial | 1.2 | 0.3 | $Bi_2S_3$ | 0.35 | 0.18 |
| Galena, from pptd. PbS | 1.2 | 0.3 | HgS | 0.054 | 0.01 |
| $SnS_2$ | 1.1 | 0.2 | | | |
| $Ag_2S$ | 0.55 | 0.14 | | | |
| SnS, crystallized | 0.14 | 0.02 | | | |

[40] *Liebig's Annalen* (1888) **249,** 326 and Emmons: *Ante*, 117.
[41] *Ztsch. phys. Chem.* (1907) **58,** 293 and Emmons: *Ante*, 117.

It is to be noted that these figures do not necessarily represent solution as sulfide, *i. e.*, equivalents of sulfide ion in solution, but rather the amount of the substance, reckoned as sulfide, that disappeared.

## Reactivity of Minerals with Various Reagents

*Sulfuric acid*, N/8, decreasing activity:[42] calcite, rhodochrosite, siderite, nephelite, pyrrhotite, leucite, tetrahedrite, labradorite, hornblende, galena, augite, sphalerite, biotite, fluorite, orthoclase, chalcopyrite, arsenopyrite, marcasite, muscovite, pyrite, quartz.

*Ferric sulfate*, M/10, decreasing activity in reduction of acidity of:[42] calcite, olivine, sodalite, rhodochrosite, siderite, pyrrhotite, leucite, tetrahedrite, galena, arsenopyrite, labradorite, sphalerite, pyrite, hornblende, enargite, marcasite, kaolinite, augite, chalcopyrite, biotite, orthoclase, muscovite, fluorite, quartz.

*Ferric sulfate*, decreasing activity in reduction of iron in:[42] pyrrhotite, siderite, tetrahedrite, arsenopyrite, galena, enargite, marcasite, pyrite, sphalerite, olivine, chalcopyrite, hornblende, orthoclase, calcite, rhodochrosite, fluorite, laboradorite, leucite, muscovite, quartz, sodalite, augite, biotite, kaolinite.

*Copper sulfate + ferric sulfate*, N/10, decreasing activity in reduction of acidity of[42]: calcite, siderite, tetrahedrite, galena, pyrrhotite, arsenopyrite, chalcocite, sphalerite, pyrite, marcasite, enargite, chalcopyrite.

*Copper sulfate + ferric sulfate*, N/10, decreasing activity in reduction of iron in:[42] (siderite), arsenopyrite, pyrrhotite, tetrahedrite, (chalcocite), galena, sphalerite, pyrite, marcasite, chalcopyrite, calcite.

When ferric sulfate and copper sulfate in solution were brought simultaneously into contact with calcite and chalcopyrite, ferric hydroxide and copper carbonate precipitated and bornite coated the chalcopyrite. Excess of ferric sulfate removed the bornite.

*Sodium bicarbonate*, 1 per cent. solution, decreasing reactivity with:[43] orpiment, stibnite, pyrrhotite, realgar, marcasite, alabandite, pyrite, stannite, tetrahedrite, smaltite, arsenopyrite, cinnabar, enargite, rosinjack, chalcocite, bornite, niccolite.

*Sodium carbonate*, 1 per cent. solution, decreasing reactivity with:[43] orpiment, realgar, stibnite, pyrrhotite, pyrite, blackjack, smaltite, marcasite, alabandite, galena, chalcopyrite, chalcocite, rosinjack.

*Potassium carbonate*, 1 per cent. solution, decreasing reactivity with:[43] orpiment, stibnite, pyrite, galena, blackjack, chalcopyrite, pyrrhotite, smaltite.

*Sodium hydroxide*, 1 per cent. solution, decreasing reactivity with:[43] orpiment, stibnite, pyrrhotite, pyrite, galena, alabandite, marcasite, blackjack.

*Carbonate Precipitation.*[44]—In solutions containing equivalent quantities of soluble salts of the metals, on addition of enough soluble carbonate to satisfy one metal only, the general order in which the metallic carbonates precipitate is: Hg, Pb, Cu, Cd, Zn, Fe, Ni, Mn, Ag, Ca, Mg. According to Kohlrausch the order of carbonate solubilities, increasing, is: Pb, Sr, Ag, Ba, Ca, Zn(?), Mg, Na, K.

*Oxidizing solutions*, order of decreasing attack by:[45] chalcocite, pyrite; chalcocite, pyrrhotite, pyrite; chalcocite, bornite, pyrrhotite, chalcopyrite, pyrite; sphalerite, chalcocite, galena, pyrite, chalcopyrite, argentite; pyrrhotite, sphalerite, galena, chalcopyrite, pyrite.

*Decreasing order of solution of sulfides in zone of oxidation* in ore deposits: sphalerite(?), chalcocite, pyrrhotite, chalcopyrite, pyrite, galena, enargite.

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[42] Nishihara: *Econ. Geol.* (1914) **9**, 743 and Emmons: *Ante*, 121.

[43] Grout: *Econ. Geol.* (1913) **8**, 427 and Emmons: *Ante*, 124.

[44] Wells: U. S. Geol. Survey *Bull.* 609 (1915) 35 and Emmons: *Ante*, 125.

[45] Several investigators, see Emmons: *Ante*, 130.

Galena is readily attacked by cold dilute sulfate solutions but the sulfate film formed protects it against further attack.

Sphalerite changes to zinc silicate in oxidation of sulfide ore deposits.

*Acid in reducing solutions*, order of decreasing attack by:[46] pyrrhotite, sphalerite, galena, chalcopyrite, pyrite.

Solutions that deposit chalcocite in secondary sulfide zones appear not to attack pyrite as long as blende is present.

*Evolution of hydrogen sulfide*, order of decreasing activity with cold dilute $H_2SO_4$:[47] pyrrhotite, sphalerite, pyrite, chalcopyrite.

*Sulfide Precipitation.*—In general the sulfide that evolves $H_2S$ most readily will most readily precipitate other metals as sulfides and will reduce acid solutions of reducible salts most readily.

Covellite replaces galena and sphalerite. Chalcocite has replaced pyrite without the intermediate step of covellite formation. Pseudomorphs of galena after zinc and iron sulfides are not common. Pseudomorphs of blende after pyrite and marcasite are unknown but marcasite after blende has been found. Chalcopyrite changes to chalcocite through a zone of covellite. Bornite likewise, probably.

Zinc sulfide is precipitated in alkaline and in very feebly acid solutions. Iron sulfide is less readily precipitated in acid solution than zinc sulfide. Oxygen tends to inhibit precipitation of copper sulfides. Pyrite apparently does not precipitate chalcocite or covellite while sphalerite is present.

Refer also to Schuerman's series, page 228.

Emmons has collected a wealth of information on the properties and behavior of the minerals of the various metals. A small part of this material, of major interest to flotation investigators, is abstracted below.

### *Copper*

At ordinary temperatures cupric sulfide is soluble in water to the extent of $3.5 \times 10^{-6}$ moles per liter (= 0.3 mg. per l.). It is insoluble, even in hot concentrated sulfuric acid, if a trace of $H_2S$ is present. Cupric carbonate is soluble 300 mg. per l. at 10° C. in water saturated with $CO_2$. Its solubility in metal carbonate solutions is very small.

Precipitation of copper sulfides, where air is excluded, may be brought about by chemical interchange with pyrite, chalcopyrite, bornite, pyrrhotite, sphalerite, galena. Oxygen tends to delay such precipitation or inhibit it entirely. Polished sections of certain ores show the sequence: pyrite → chalcopyrite → bornite → covellite → chalcocite. Excess of acid (sulfuric) tends to inhibit the precipitation of copper sulfides on pyrite and chalcopyrite. Native sulfur will precipitate the copper sulfides from copper sulfate solution. Bornite reacts with cupric sulfate to produce a film, which is probably covellite, and which changes subsequently to the color of chalcocite. Chalcopyrite is not readily affected by cupric sulfate alone, but with ferrous sulfate the chalcopyrite is filmed, and finally changes to the color of covellite. With ferric sulfate present, copper sulfide is precipitated from copper sulfate solutions slightly, if at all, due to the fact that ferric sulfate is an active solvent of nearly all natural sulfides. In dilute alkaline solutions, carbonate, hydrate or silicate, many metallic sulfides react to form alkaline sulfides and these react with cupric sulfate to precipitate cupric sulfide. Chalcocite is formed on pyrite and chalcopyrite more readily in alkaline environment. Copper sulfate attacks the sulfides of all metals below copper in Schuerman's series (see p. 228), precipitating copper sulfide. Chalcocite will precipi-

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[46] Emmons: *Ante*, 137.

[47] *Idem*, 150.

tate gold and silver from chloride and sulfate solutions. Covellite replaces sphalerite more rapidly than it does pyrite, but less rapidly than it does pyrrhotite.

*Lead*

Solubilities: Sulfate, 41 mg. per l.; chloride, 14,900 mg. per l.; carbonate, 1 mg. per liter.

One gram of galena in contact with sulfuric acid and ferric sulfate gained 0.17 g. in 81 days by oxidation; in acid solution alone the gain was 0.07 g.[48]

Some samples of galena yield $H_2S$ in dilute $H_2SO_4$, but the action is not sustained. It is not unlikely that this is due to MnS in the galena.

*Zinc*

Solubilities, Mg. per l.: sulfate, 531,000; chloride, 2,039,000; carbonate, 40; nitrate, 1,178,000; sulfide (freshly precipitated), 7.

Sphalerite dissolves in sulfuric acid, more readily in the presence of ferric sulfate. It oxidizes slowly in the absence of pyrite. Being the most soluble of the ordinary metallic sulfides it cannot replace the others; *e. g.*, Cu, Ag, Pb. It is replaced by $Cu_2S$, CuS, $Ag_2S$ and PbS.

Zinc salts hydrolyze but not so readily as ferric salts.

*Aluminum, Silica*

$$2NaAlSiO_4 + 2H_2CO_3 + 3H_2O = Al_2O_3.2H_2O + H_2Na_2(CO_3)_2 + 2H_2SiO_3$$

$$\underset{\text{(kaolin)}}{H_2Al_2(SiO_4)_2.H_2O} + \underset{\text{(strong)}}{3H_2SO_4} = Al_2(SO_4)_3 + 2H_2SiO_3 + 3H_2O$$

The above reaction probably takes place slowly under geological conditions.

Acid waters become alkaline on prolonged contact with rocks containing alkaline silicates.

Silica is dissolved by acid waters, but more readily by alkaline.

## Collecting Agents

Taggart, Taylor and Ince[49] gave qualitative evidence that when galena is prepared for flotation with thiocresol, there is chemical reaction between the galena particles and the organic compound. During the past year the surface of galena particles, produced by grinding in air, in water in contact with air, and in nitrogen atmospheres, has been investigated.

## Oxidation of Galena

When galena is dry-ground in air or in water impregnated with air, the newly formed sulfide surfaces are quickly changed into oxidized lead compounds. Lead sulfate ($PbSO_4$), one or more less oxidized sulfur-oxygen compounds of lead ($PbS_mO_n$, where the ratio $n/m$ is less than 4), and lead carbonate, are the probable salts. The evidence for these statements follows:

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[48] *Jnl. Geol.* (1913) **21**, 11.

[49] *Ante.*

*Lead Sulfate.*—1. When galena, either dry-ground or wet-ground, is shaken with distilled water and filtered, the filtrate gives a precipitate with barium chloride, which precipitate is not soluble in an excess of hydrochloric acid. It should be noted that the amount of lead sulfate in solution is well below the saturation limit.

2. When galena is shaken with a solution of potassium xanthate (or of thiocresol) the xanthate (or thiocresylate) radical is abstracted and sulfate radical (proved as in 1) is thrown into solution. Xanthate ion is tested for by measuring the reducing ions in the solution, as below. The amount of sulfate ion recovered in this experiment is well in excess of that found in (1) above.

3. Potassium chromate, which, like the xanthate, forms a very slightly soluble lead salt, behaves similarly with ground galena, giving up chromate ion and increasing the sulfate content of the solution. For determination of chromate content of the test solutions we made colorimetric comparison with solutions of known concentration of $K_2CrO_4$ and also oxidation of iodine, according to the ionic equation

$$14H^+ + Cr_2O_7^{=} + 6I^- \rightleftharpoons 2Cr^{+++} + 6I^\circ + 7H_2O.$$

*Lead Sulfite, Etc.*—1. When galena is shaken with distilled water and filtered, iodine titrations on the filtrate show the same reducing power as distilled-water blanks. That is to say, the sulfite, etc., are not soluble in water to an extent within the sensitiveness of the iodine titration.

2. Galena was treated with potassium xanthate solution, then filtered. The filtrate was treated with an excess of acetic or tartaric acid to convert any residual xanthate into xanthic acid. The mixture was then extracted with petroleum ether, with which xanthic acid is miscible. The residual water contained reducing ion, whose quantity was now determined by iodine titration. Another portion of the filtrate was treated as above to remove xanthates. Hydrogen peroxide was added, after which the solution gave a barium chloride test for sulfates much greater in intensity than the direct sulfate test previously described. Another portion of the extracted filtrate gave a negative test for sulfide ion (see below).

3. To the filtrate from a xanthate-solution treatment of galena, after removal of residual xanthate (see preceding paragraph 2), was added silver nitrate or silver acetate. Blackening occurred. In the absence of sulfide ion, previously proved, this evidences thionates and probably thiosulfates.

4. The filtrate from the treatment of galena with sodium chromate solution shows reducing ion when titrated with iodine. This titration may be made in the presence of residual chromate ion, if hydrogen-ion concentration is kept low enough.

5. Potassium oxalate ($K_2C_2O_4$) acts the same as the chromate.

*Lead Carbonate.*—1. When galena is treated with xanthate solutions of about five times ordinary flotation concentrations, the residual solution develops measurable alkalinity. The amount of alkalinity thus developed was quantified in terms of potassium carbonate by an experimental calibration curve. The amount of carbonate thus determined corresponded, in order of magnitude, to the amount of lead carbonate required to react with the amount of xanthate abstracted in excess of that accounted for by sulfate and the reduced sulfur-oxygen ($S_mO_n$) ions. We believe that the lack of closer agreement (see Table 1) is due in great part to the extreme difficulty of making pH measurements in carbonate solutions.

TABLE 1.—*Tests on Abstraction of Potassium Xanthate by Galena*

| Test | Original Solution, Potassium Xanthate, Mg. per Liter | Potassium Xanthate Removed, Mg. per 100 Grams Galena | | | | Alkalinity, pH | |
|---|---|---|---|---|---|---|---|
| | | Total, Mg. per 100 G. Galena | Accounted for as | | Unaccounted for | Actual Filtrate | Control Solution[a] |
| | | | Reduced Divalent Sulfur-oxygen Ions | Sulfate Ion | | | |
| A | 10 | 6.5 | 1.3 | 5.5 | 0 | 6.95[c] | 6.43 |
| B | 30 | 7.7 | 1.5 | 5.5 | 0.7 | 7.05[c] | 6.48 |
| C | 100 | 28.1 | 1.9 | 4.9 | 21.3 | 7.52[b] | 6.54 |
| D | 150 | 27.4 | 1.8 | 6.3 | 19.3 | 8.10[b] | 6.86 |
| E | 200 | 36.6 | 4.8 | 8.4 | 23.4 | 9.25[b] | |
| F | 300 | 28.6 | 2.1 | 6.0 | 20.5 | 8.15[b] | 7.00 |

[a] Potassium xanthate blanks.

[b] The alkalinity of potassium carbonate solutions of strengths corresponding to the decomposition product, by a carbonate, of the corresponding amounts of xanthate in the "unaccounted" column, was pH = 9.2.

[c] Corresponding pH tests on standard carbonate solutions not made on account of utter lack of dependability at these low concentrations.

Results of a series of abstraction tests with xanthate solutions of different strengths are given in Table 1.

*Lead Sulfide.*—The methylene blue test[50] for sulfide ion, sensitive to 0.06 mg. per l. of water, which we proved may be made in the presence of xanthate ion, was used.

[50] Take 10 c.c. of the solution to be tested in a colorimetric tube. Add 1.5 c.c. of 3-molar or 4-molar $H_2SO_4$ and dilute to about 45 c.c. Add 1 c.c. of a 2 per cent. aqueous solution of p-phenylene-dimethyl-diamine hydrochloride and 1 drop of 5 per cent. ferric chloride solution. Mix well, dilute to 50 c.c. and allow to stand until color change ceases. Compare with solution of known concentration. The red color of the reagent turns to a permanent blue in the presence of sulfide ion. The blue precipitate falls gradually if the solution is too concentrated in sulfide ion. Sulfites give a purple color which develops slowly and is not permanent.

No sulfide ion was detectable either in distilled-water or xanthate extraction of galena.

*Coating of Galena.*—Galena (−200-mesh dry-ground) that had been treated with an excess of aqueous potassium xanthate solution (100 mg. per l.) and then washed in water, was extracted with (*a*) alcohol and (*b*) alcohol plus benzol. When the extracts were mixed with water and distilled to remove the organic solvent, there was a precipitate of silky needles (indicative of lead xanthate). These were dissolved in hydrochloric acid, the solution evaporated to drive off xanthic acid (indicated by the characteristic odor), sodium acetate was added to neutralize the residual hydrochloric acid, then sodium chromate. A yellow precipitate indicated lead. A portion of the acetate solution blackened on addition of sodium sulfide, also indicating lead. Another portion of the silky precipitate from the organic-solvent extract was made strongly alkaline with sodium hydroxide, which dissolves lead xanthate, an equivalent amount of hydrochloric acid was added, then cuprous ion, when there was a yellow precipitate, accepted to be cuprous xanthate.

A solution of sodium xanthate from which xanthate ion equivalent to 25 mg. of sodium xanthate per 100 g. of galena had been abstracted, was tested for sodium ion and showed no determinable removal. (Sensitivity of analytical method, ±1 per cent. on the amount present.)

When zinc ethyl xanthate solution (solubility of the zinc salt is 335 mg. per l.) was used instead of sodium xanthate with galena, xanthate ion was abstracted but zinc ion was not.

*Wet Grinding.*—Qualitative tests for sulfate and reduced sulfur-oxygen ($S_mO_n$) ions and for alkalinity (indicating $CO_3^=$) were made on galena ground under water exposed to the atmosphere (duplicating mill grinding). The results were the same as on dry-ground galena.

### *Rate of Oxidation of Galena*

Fig. 2 shows the rate at which removal of xanthate ion by galena increases with time of exposure of the galena to air, after grinding and before treatment with potassium ethyl xanthate solution. Since previous experiments indicate that all xanthate ion that disappears from solution is removed by metathesis with oxidized lead salts, the ordinates of the curve are proportional to the extent of oxidation of the galena, and the curve may, therefore, be read as indicating the rate of oxidation of galena in air.

The experiments were performed on −200-mesh galena, freshly ground from large lumps. The xanthate solution contained 200 mg. of potassium ethyl xanthate per liter and the proportion of galena to solution was 1:10. Galena and solution were shaken together for 1 hr. in each experiment. The graph is a typical rate-of-reaction curve, and confirms

the conclusion previously expressed that galena surfaces react chemically with constituents of the atmosphere, or of the solutions in which they are ground, to form coatings of oxidized lead minerals at their surfaces.

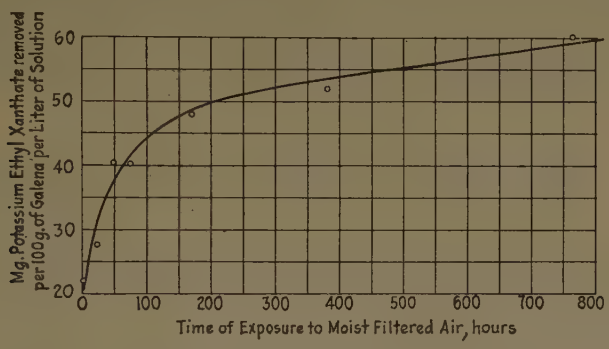


FIG. 2.—REMOVAL OF POTASSIUM XANTHATE BY GALENA.

*Variation in Xanthate Abstraction with Concentration of Solution*

Fig. 3 shows the results of a series of abstraction tests in which freshly prepared −200-mesh dry-ground galena was treated with potassium ethyl xanthate solutions of different strengths. The curve shows maximum utilization of the added xanthate with minimum addition. Thus with a solution strength of 12.5 mg. per l., corresponding to 0.1 lb. xanthate per ton of ore in a pulp containing 20 per cent. solids, upwards of 10 mg. of xanthate was removed or over 80 per cent. of that added. At 25 mg. per l. (0.2 lb. per ton) 60 per cent. of the added xanthate was abstracted, and at 62.5 mg. per l. (0.5 lb. per ton) only 40 per cent. was removed.

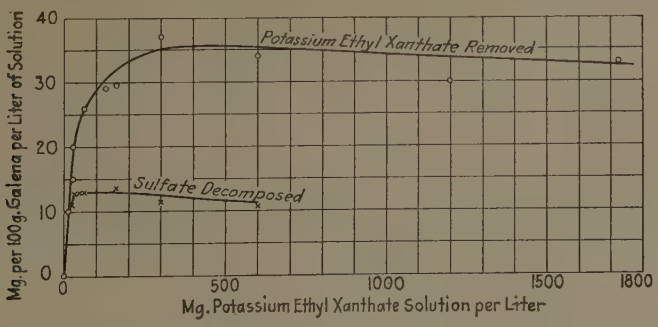


FIG. 3.—RELATION BETWEEN SURFACE REACTIONS AND REAGENT CONCENTRATION.

The curve also shows a maximum at a solution strength near 500 mg. per l. This is probably due to the fact that lead xanthate is soluble in solutions of potassium xanthate, the solubility increasing with the concentration of the latter salt.

Fig. 3 shows also the amount of sulfate ion, reckoned in terms of potassium ethyl xanthate decomposed, thrown into solution by the reaction of xanthate with lead sulfate. The curve for solution strengths beyond 25 mg. per l., is probably to be considered horizontal, which means that the relatively soluble sulfate is the first of the lead salts to be decomposed by the xanthate, and that decomposition of the other lead salts is substantially nil until the sulfate is all used up.

### *Effect of Solubility of Surface on Xanthate Removal*

If galena is first treated with a soluble chromate (p. 232), which forms a much less soluble surface coating on the galena particles than that formed by oxidation, and then with xanthate solution, xanthate removal is reduced to about 25 per cent. of normal. This explains why chromates lessen the floatability of galena with soluble collecting agents (but does not explain the action with oil collectors, be it noted).

### *Grinding in an Atmosphere of Nitrogen*

When galena is dry-ground in a neutral atmosphere, specifically nitrogen, and then subjected to air-free xanthate solution, likewise in a nitrogen atmosphere, xanthate removal is decreased from some 25 mg. per 100 g. galena to from 5 to 10 mg. The obvious explanation of this dimunition in xanthate abstraction is that the lump galena was already oxidized, but xanthate removal by the lump galena was only 2 mg. per 100 g. The following facts throw some light on the apparent discrepancy:

Tests designed to investigate grease contamination of galena surfaces have shown that air-borne grease has already contaminated over 90 per cent. of the cleavage surfaces formed in breaking down a 3 or 4-in. cube of galena to ⅛ to ¼-in. cubes. From this it may be inferred that oxidation has similarly progressed to an appreciable extent on cleavage planes within a lump, prior to breaking down the lump. Furthermore, polished sections of ores in the zone of oxidation commonly show visible alteration proceeding apparently entirely surrounded by unaltered material. It must be admitted that, with respect to such evidence, access to the attacking reagent in these cases may have been by passages out of the plane of the section.

While the nitrogen experiment, therefore, does not prove conclusively that grinding in a neutral atmosphere prevents the formation of galena-particle surfaces that will abstract xanthate, and hence that abstraction is dependent on prior oxidation of the galena surfaces, or at least upon the formation thereon of lead compounds more soluble than the sulfide, it does point strongly to such a conclusion.

*Relation of Xanthate Removal to Galena Surface*

Galena, −10-mesh + 65-mesh, freshly broken in air, abstracted 2 mg. potassium ethyl xanthate per 100 g. of galena while −200-mesh galena abstracted 16 mg. of xanthate per 100 g. of galena from the same solution. This is evidential, if further evidence is needed at this late date, that the alteration of the floatable particles is a surface phenomenon.

*Abstraction Tests with Sphalerite*

*Water.*—When sphalerite is shaken with water, the water becomes slightly acidic (pH = 6.33) and the water gives a strong test for sulfate (with acidified $BaCl_2$).

*Potassium Ethyl Xanthate.*—When sphalerite is treated with xanthate and the extent of abstraction of xanthate ion is tested by the usual iodine-titration method, the results indicate almost negligible removal of xanthate. When however, the filtrate is acidified and the resulting xanthic acid removed by petroleum ether, the residual solution has reducing action, and when the iodine consumed by this solution is taken into account, it is found that −200-mesh sphalerite will abstract xanthate ion equivalent to about 5 to 10 mg. of potassium ethyl xanthate per 100 g. of solid from a solution containing 100 mg. of ethyl xanthate per liter.

Our interpretation of these facts is that sphalerite oxidizes in air (and probably in oxygenated water) to form one of the reduced sulfur-oxygen compounds, $ZnS_mO_n$ ($n/m < 4$) and that this compound reacts with the alkaline xanthate to form zinc xanthate and $K_2S_mO_n$. But the solubility of zinc xanthate is about 335 mg. per l. Hence this compound dissolves to a considerable extent from the sphalerite-particle surfaces, with the result that the abstraction test shows low removal.

The behavior of sphalerite with soluble collectors appears, then, to be analogous to that of galena, *viz*: first oxidation of the sulfide, and subsequently a double-decomposition chemical reaction between the oxidized surface compound and the organic collector, resulting in the formation of a relatively slightly soluble salt of the base-metal cation with the organic anion. (Evidence for orientation of the resulting compound at the solid surface is given by Taggart, Taylor and Ince.[51])

The difference in abstraction from that by galena, which difference is reflected in a marked difference in the collecting index of xanthate on the two minerals brings out the fact that in order for an organic reagent to be a satisfactory collector for a given mineral, the organic salt formed with the base-metal cation must have a very low solubility. Other evidence presented later (p. 242) indicates that the order of solubility of this salt must be in the neighborhood of less than 1 mg. per l. It will also be apparent from the reasoning that its solubility must be less

[51] *Ante.*

than that of either of the entering reactants; *i. e.*, the collecting agent and the mineral forming the surface of the particle to be floated.

The Research Staff of United Verde Copper Co.[52] showed by analyses of solutions taken at different points in the United Verde mill that the oxygen content of the mill waters decreased from the point where the waters entered the mill up to the point of introduction into the flotation machine, and that the $S_mO_n$ ion ($n/m$ up to and including 4) increased up to the same point. This indicates that the iron and copper sulfides in the Clarkdale pulp oxidize in a similar manner to the lead and zinc sulfides that we have studied.[53]

## Brownian Movement

We have found that there is remarkable parallelism between Brownian movements of the various mineral particles in flotation pulps and the flotation behavior of these minerals. The initial discovery prompted an inquiry into the mechanism of Brownian movement itself, in the hope that therefrom light would be thrown on the mechanism of flotation. The result of the inquiry and concurrent experimentation was, in our opinion, to disprove the classical explanation for Brownian movement, and to lay the basis for an alternative hypothesis of mechanism that fits all of the facts in our possession, and that is highly useful in interpretation of flotation phenomena.

When certain finely divided substances are suspended in certain fluid media, and the suspension is examined under sufficiently high magnification to resolve the smaller particles clearly, the mass of fine particles is seen to be in erratic motion, which, for any particle that is moving, is continuous and which continues more or less indefinitely, so long as surrounding conditions remain reasonably constant. The name of this movement comes from its discoverer.

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[52] O. C. Ralston et al. See page 369.

[53] The authors of the United Verde paper give figures for sulfide ion in the pulps. This disagrees with our experience. The United Verde method of determining sulfide ion was to titrate one portion of mill solution with iodine and another with permanganate and to accredit the difference in reducing power, as determined by the two standard oxidizers, to sulfide ion, on the theory that sulfide ion will reduce permanganate but not iodine. Soluble sulfides in alkaline or in acid solution will reduce iodine. (See Treadwell and Hall: Analytical Chemistry, 1921 ed., **1**, 358.) Permanganate titrations in solutions of such low concentration of $H^+$ as were used at United Verde (pH = about 4) are highly erratic and unreliable, because at this acidity, even if maintained constant throughout the titration, permanganate ion reduces to manganous ion and manganese dioxide in undetermined and therefore unknown proportions. In order that the oxidizing effect of permanganate may be accurately calculated from consumption of permanganate ion, titration must be performed at pH = $\pm$ 0.6, corresponding to N/2 $H_2SO_4$. Here permanganate ion reduces almost exclusively to manganous ion. Consequently we do not consider the United Verde results to be read as indicative, even, of the presence of sulfide ion in the mill pulps.

## Classical Theory

The classical explanation of Brownian movement is that the particles are being continually bombarded by the molecules of the suspending fluid, and that so long as the mass of the particles is small enough and the momentum (mass × velocity) of the bombarding molecules great enough, the motion will continue.

It has been found by experiment that the motion in any given case can be stopped by the addition of small quantities of certain electrolytes. It has also been observed that such cessation of motion is frequently accompanied by aggregation of the particles (flocculation). And it has been further observed, in the case of many suspensions which show movement, that the particles migrate in an electric field, from which it has been concluded that they carry electrical charges.

On the basis of these observations, the dispersion that permits the particles to remain as individuals small enough to respond to molecular bombardment has been accredited to electrostatic repulsion by the charges on the particles. The charging has been accredited to preferential adsorption of certain ions from solution in the suspending medium. Flocculation has been said to be induced by the added electrolyte, which, by some means, discharged the particles, after which discharge they immediately flew together, as it were, under the influence of some more or less mysterious forces: "like-to-like," gravitational attraction, molecular attraction, etc. *ad nauseam.* And once flocculation had occurred, the particles were, of course, too large for molecular bombardment to have any visible effect thereafter, consequently movement ceased.

### *Experimental Work on Brownian Movement Mechanism*

1. A suspension of quartz, cleaned with great care, ground in porcelain to pass 200-mesh, then ignited at 1000° C., is in vigorous movement in M/1000 sodium carbonate solution and at rest in M/1000 sulfuric acid solution.

(*a*) A slide was made[54] of the suspension in carbonate solution;

[54] The technique of slide preparation is a large part of the battle. Selected extra-thin slides and thin cover-glasses are soaked in chrome-acid solution for several hours, then placed in running tap water, then in running distilled water, and partially dried between clean filter papers. All handling is done with clean forceps. A drop of the suspension is then placed on the slide, the cover-glass put on, excess liquid at the edge blotted away, and the cover-glass sealed on by rapid strokes of a camel's hair brush wet with melted paraffin. (Paraffin is used because of its insolubility in water and consequent lack of effect on the suspension.) The microscopic examination is made with a No. 9 fluorite lens (dry) and a special dark-and-light-field condenser (oil-immersion), which permits instantaneous change in the type of illumination. Magnifications from 2500 to 3400 are best.

leaving portions of the periphery of the cover-glass at opposite ends of the slide unsealed. The quartz was in active movement. A drop of M/500 sulfuric acid was placed at each of the unsealed places. Diffusion of acid into the carbonate preparation started at once. The progress of the acid could be followed across the slide, using a low-power (16-mm.) objective. In this field the particles on the side toward the advancing acid were at rest, the balance in motion. The preparation was made of such density that a field appeared like Fig. 4, when viewed at 2500 dia. At this magnification it was easily possible to observe cessation of movement of the particles. They first slowed down, seemed to settle, strike bottom (the slide) perhaps give one or two spasmodic wriggles, perhaps even go into suspension again for a few seconds, but eventually each settled down and stopped. There was no slightest agglomeration (flocculation) and no visible change of any kind in the particles, other than from a state of motion and suspension to one of rest and non-suspension.

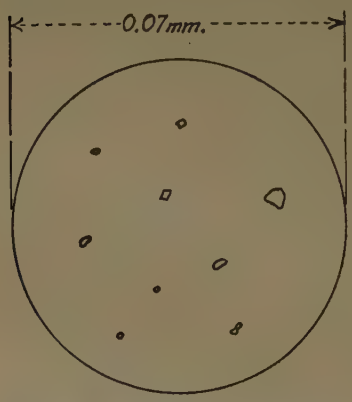


FIG. 4.—DIAGRAMMATIC SKETCH OF FIELD WITH QUARTZ SUSPENSION.

It seems from this that the change from motion to rest was not due to any increase in mass of the particle.[55]

If the classical theory is to hold, then, there must have been a decrease in the momentum of the water molecules. We have, of course, no direct knowledge of either the active masses or their velocities, but we do know that viscosity is, in a general way, a measure of the molecular activity of a substance, at least to the extent that, for any given substance, molecular activity is greatest and viscosity least in the gaseous phase, both are intermediate in the liquid phase, and viscosity greatest and molecular activity least in the solid phase. In the liquid phase, viscosity decreases with increasing molecular activity when a liquid is heated. Since, therefore, there are no marked differences in viscosity of aqueous solutions for changes in the concentration of inorganic solutes within the limits of M/500 and M/1000 concentration, the apparent conclusion is that there are no great changes in molecular activity of the water.

We contend, in the light of these showings, that the classical theory cannot hold, and that we must seek elsewhere than in bombardment by

[55] If it be claimed that there was change in mass due to attachment of something invisible on to the particles, then the change for the smallest particles pictured in Fig. 4 must have been to a volume greater than that of the largest, since all moved initially. Or else the further assumption must be made that the added mass, in addition to its invisibility, has likewise an inexplicably high specific gravity.

the water molecules for explanation of the movement of the quartz particles.

The experiment was continued by next adding M/500 sodium carbonate solution to the slide. A wave-front of particle motion now passed across the slide, until the whole field was again in motion, more sluggish than in the first place, but nevertheless unmistakable.

A preparation of quartz in M/1000 sodium sulfate with a slight excess of sodium carbonate had motion slightly greater than that of the revivified slide.

The same process of stopping and revivification was performed in a test-tube, the process being followed by slides prepared at intervals. Here there was some flocculation observed in the slide made from the acidified water and this flocculation had not wholly disappeared on the slide made from the suspension over-neutralized with sodium carbonate, but some of the floccules in this last slide were in sluggish motion, while the small individuals moved freely in suspension. This latter fact evidences that the same forces act on both large and small particles, but with the responses inversely proportional to the sizes.

Revivification such as this, of particles in solutions of increased concentration of inorganic solutes, and consequently of increased viscosity, as compared to the solutions in which the particles were at rest (assuming a small viscosity change, although unmeasurable), confirms the previously stated conclusion against the classical theory.

### *Proposed Hypothesis for Brownian Movement*

It is the opinion of the authors that particles in colloidal suspension, which, therefore, are in Brownian movement, are ionized at the surface, with one of the ions preponderantly anchored to the particle surface, the other being free-swimming; that the suspension of the visible particle is due to the mean pull on it of the surrounding swarm of free-swimming ions, which are in turn maintained dispersed by whatever forces induce ionic solution; that motion of the visible particles is due to unbalanced vibration, as it were, between the ionized and unionized states, taking place at random over the entire surface of the particle;[56] and that the visible particles do not coalesce for the same reason that ions of the same element in ionic solutions do not coalesce.

The essentials for dispersion and movement are: (1) sufficient ionization of the surface and (2) anchoring of one of the ions to the particle. If ionization is insufficient, there are not enough free-swimming ions to hold up the visible particle. If the surface compound is too soluble,

[56] So far as this phase of the hypothesis is concerned the reasoning is similar to that by which the concept of molecular bombardment was translated into the idea of visible movement.

neither ion is sufficiently anchored to transmit motion to the suspended particle.

When motion is halted and flocculation occurs, the explanation, under the present hypothesis, is that either one of two things has occurred: (1) surface ionization has been almost completely suppressed, or (2) solubility has been markedly increased and anchorage of ions to the particle surface correspondingly lessened. As a result, the repulsive forces between particles are lessened to the point that random contacts are not prevented thereby. When such random contacts occur, the particle-solution interface for the system is at a minimum and subsequent separation would require work to be done against the interfacial forces. In the absence of such work the contact persists and the result is a floccule.

### *Experimental Evidence for the New Hypothesis*

A suspension of dry-ground galena[57] freshly mixed with distilled water and promptly examined[58] shows no Brownian movement. A suspension in M/1000 sodium carbonate solution is in vigorous movement; in M/1000 potassium dichromate does not move; in M/1000 hydrochloric acid or nitric acid there is no movement; in M/1000 sodium hydroxide or ammonium hydroxide there is movement.

We start with the information already available (p. 231) that an aged surface of dry-ground galena is changed more or less completely to lead sulfate, $PbS_mO_n$ ($n/m < 4$), and (probably) lead carbonate. Lead sulfate, soluble to the extent of 40 mg. per l., is probably the most soluble of these surface salts, as evidenced by the fact that it is the one first displaced by xanthate (p. 235). But its solubility is so great that it can break loose to a certain extent, at least, from the surface, as evidenced by the fact that distilled water alone will extract sulfate (p. 232). We have no information as to the solubility of the $PbS_mO_n$ salts except that inferred in the statement of the relative solubility of the sulfate above. The solubility of the carbonate is given as 1 mg. per l. (p. 231). In sodium carbonate solution, sulfate and $S_mO_n$ ions are displaced to a considerable extent by carbonate ion and the surface becomes largely lead carbonate. By the change from a relatively soluble to a relatively insoluble surface, motion is induced.

Powdered lead carbonate in potassium dichromate and in potassium xanthate solutions turns yellow, indicating precipitation of lead dichro-

[57] All of the preparations discussed under this section were made from pulverized samples of selected pure minerals, dry-ground in air in a porcelain mill with flint pebbles, screened through a 200-mesh sieve, and thereafter kept in glass containers not tightly sealed. Therefore, they may be considered as thoroughly oxidized (see page 20), although there is no visible alteration.

[58] Not over 15 min. should elapse between mixing the mineral and water and microscopic examination, if this description is to apply.

mate and lead xanthate respectively, which is to say that these salts are less soluble than the carbonate. And, as stated above, in solutions of dichromate and of xanthate ions, motion of galena particles ceases.

Chlorides and nitrates of lead are even more soluble than the sulfate. Lack of motion in chloride and nitrate solutions is, therefore, in accord with the hypothesis.

The hydroxides would tend to change sulfates, sulfites, etc. into basic compounds with the same acid radical, with consequent decrease in surface solubility.

On the score of anchorage of one of the ions, it is illuminating that while distilled water extracts some lead sulfate from galena, it leaves much more behind, which may be subsequently displaced by the xanthate. Yet the solution of sulfate in the distilled water extraction test is far from saturated. That is to say, distilled water can tear away far less than all of the sulfate, even though the solution formed is far short of saturation. Zinc sulfate, which is much more soluble than lead sulfate, goes into solution from sphalerite surfaces to a much greater extent than lead sulfate from galena surfaces. Zinc sulfide, which is only slightly soluble (about 7 mg. per l.), is not extracted by distilled water. From which it may be concluded that the degree of anchorage of one of the ions of one of these surface coating compounds is generally proportional to the insolubility of the compound.

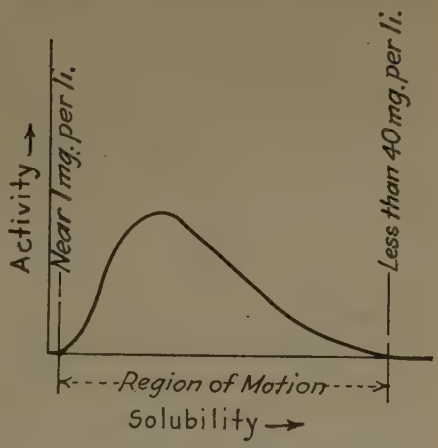


FIG. 5.—RELATION BETWEEN BROWNIAN ACTIVITY AND SURFACE SOLUBILITY.

On the basis of these data, it is thought that some relation between motion and surface solubility (and ionization) such as is shown in Fig. 5 exists.

*Experimental Correlation of Brownian Movement and Flotation*

A series of tests was run in which to a suspension of each of the four minerals, galena, sphalerite, pyrite and quartz in distilled water there were added successively sodium carbonate, potassium cyanide, zinc sulfate, potassium xanthate, pine oil and copper sulfate in the proportions usual in flotation. That is to say, when the xanthate, for example, was added to one of the suspensions, there were already present sodium carbonate, potassium cyanide and zinc sulfate. After each addition of reagent a slide was made and examined at 2500 diameters.

*Galena* was somewhat flocculated and substantially at rest in distilled water; dispersed and in motion after the carbonate and cyanide additions; zinc sulfate had little or no effect on the motion; xanthate stopped the motion entirely and there was more flocculation; pine oil and copper sulfate caused no further change.

*Sphalerite* was somewhat more dispersed than galena in distilled water but was not in motion; the carbonate increased the dispersion and started motion; cyanide increased the motion and successive additions of zinc sulfate, xanthate and pine oil produced no change. Copper sulfate stopped motion and produced some flocculation.

*Pyrite* was flocculated and motionless in distilled water. Movement began with the carbonate addition, increased with cyanide and was not stopped even by copper sulfate.

*Quartz* was in motion throughout.

It will be noted that there is complete correlation here between Brownian movement of the various minerals and their behavior in differential flotation, and as a first approximation we may set up the conclusion that particles in Brownian movement will not float.

But we can go further than this. In the hypothesis set up to explain Brownian movement it was postulated that, for Brownian movement to occur, the particle surface must be ionized and one of the ions anchored to the surface. Such a condition means, of course, that the surface is one that tends to disperse itself through water, to surround itself by water, to become and remain wet by water, to be water-avid, in other words, and consequently non-floatable.[59] To overcome this state and render the particle floatable, we must anchor a water-repellent film at the surface. Such a film must be un-ionized, and therefore, on the hypothesis, cannot cause Brownian movement.

If we examine the behavior of the various particles in the various solutions from the point of view of possible chemical reactions, and in the light of these hypotheses, there are some interesting concordances.

*Galena* in distilled water has, we have seen, a coating of $PbSO_4$, $PbS_mO_n(n/m < 4)$ and (probably) $PbCO_3$. It is charged positively,[60] which means that lead is the anchored ion. Addition of sodium carbonate displaces sulfate and sulfite ions, because of the lesser solubility of lead carbonate, giving a coating of closely held carbonate ions (arguing that slight solubility means tight or close holding), and these cause vigorous movement. Addition of cyanide causes no change in the surface coating because neither of the possible products of reaction with lead carbonate is less soluble than the carbonate. The same is true

[59] Taggart, Taylor and Ince. See page 285.

[60] Don O. Noel, in the experimental work for his thesis at Columbia in 1929, checked over Ince's work (p. 261) and found that Ince was probably in error in rating galena in distilled water negative.

of zinc sulfate. But xanthate ion forms with lead a less soluble lead compound (lead xanthate) than the carbonate. Hence potassium xanthate reacts with the carbonate, displacing the non-anchored ion and forming un-ionized lead xanthate. (Lack of ionization is inferred from the fact that a water-repelling coating is formed.[61]) Pine oil contains no constituents that can decompose lead xanthate. Copper sulfate reacts with lead xanthate to form cuprous xanthate, which is less soluble than lead xanthate, but the reaction is very slow, due to the very slight solubility of the lead salt, and it is not unlikely that equilibrium is reached with a large percentage of the lead xanthate unaffected. Hence galena floats in the presence of the copper salt and fails to show Brownian movement.

*Sphalerite* ground in air has a surface largely $ZnSO_4$ and $ZnS_mO_n$ ($n/m < 4$). In distilled water both of these salts are apparently too soluble to produce Brownian movement. Sodium carbonate produces a coating of $ZnCO_3$, the solubility of which is given in the books as from 10 to 40 mg. per l. This means an ionized and fairly closely held surface coating with consequent movement. Zinc cyanide is rated as insoluble and will precipitate from zinc carbonate solution, hence cyanide ion displaces carbonate ion at the sphalerite surfaces. But the fact of Brownian movement, on the hypothesis, indicates an ionized surface. Zinc sulfate should have no chemical effect, except, perhaps, a small one on the solubility of the cyanide. Zinc xanthate with a solubility of 332 mg. per l. will not, of course, replace the cyanide at the sphalerite surface, therefore no water-repelling coating can form and no flotation occurs.

*Copper sulfate* stops Brownian movement of the sphalerite particles and renders them floatable with xanthate. This means, according to the new Brownian movement hypothesis, that the copper sulfate reacts with the surface layer of zinc cyanide on the particles to render the surface either insoluble in the copper solution or relatively highly soluble. We have not, at present, experimental determination of what the reaction is. Several plausible hypotheses may be built up on the known reactions of the various constituents present, however. One such follows: According to Mellor[62] an excess of cupric salts reacts with soluble cyanides to form first cupric cyanide and then cuprous cyanide, both of which are rated as insoluble. On the assumption that cuprous cyanide is less soluble than zinc cyanide, copper sulfate would react with zinc cyanide giving a surface of zinc sulfate and a precipitate in the pulp of cuprous cyanide. The excess of copper sulfate would react with the sphalerite particle surface now to form cupric sulfide which either reacts directly with xanthate to form an insoluble and water-repellent xanthate surface, or the cupric sulfide first oxidizes slightly and then reacts. We have evidence of the

[61] See Taggart, Taylor and Ince: *Ante.*

[62] A Comprehensive Treatise on Inorganic and Theoretical Chemistry, **3.**

former reaction in the fact that a water-repellent xanthate surface will form[63] on sphalerite particles that have been soaked in copper sulfate solution, when these are placed in xanthate solution saturated with hydrogen sulfide. Comparative solubility tests indicate that cupric sulfide and cuprous xanthate are very close together in solubility in water.

*Pyrite* ground in air and placed in water introduces thereinto sulfate, ferric and ferrous ions, indicating the formation of ferric and ferrous sulfate at the pyrite-particle surfaces. Both salts being relatively highly soluble, the particles do not have Brownian movement. Sodium carbonate changes the surface to ferrous carbonate, rated as insoluble, but, since the particles are in motion the surface is ionized, according to our hypothesis. We have, as yet, no knowledge of the progressive reaction or lack of reaction with potassium cyanide, zinc sulphate, copper sulfate and potassium xanthate, except that the final coating, whatever it may be, is still soluble, as indicated by the movement of the particles, and therefore, water-avid, which explains the lack of flotation.

*Quartz*, which is in movement throughout, is thereby indicated to maintain a water-avid and, therefore, non-floatable surface throughout. It is our opinion that, notwithstanding the care taken in preparation of our sample, there was probably sodium silicate or sodium hydrate present, and that the motion which we observed first, in distilled water, was due to an ionized surface of sodium silicate, the silicate being the anchored ion and imparting a negative charge.

It is interesting to note that the addition of lime to the quartz suspension stopped the motion and rendered the particles electrically neutral. This indicates formation of un-ionized calcium silicate at the particle surfaces.

Quartz, even though it is stopped by lime, will not float with xanthate, because the surface layer does not react to form an insoluble, water-repelling xanthate surface.

Determination of the details of all of the chemical reactions at particle surfaces in a complex ore pulp would require long, slow and painstaking experimental work. Even under the simplified and controlled conditions of the laboratory, much remains yet to be done. But the accord of the experimental work thus far with the general hypothesis that chemical reaction is controlling in collection has been so remarkable, and the new hypothesis of Brownian movement has been so useful as a tool in exploring surface reactions, as to justify publication now, notwithstanding the uncompleted detail.

## Summary

1. It is postulated that, in flotation with soluble reagents, all phenomena governing collection are controlled through simple chemical

[63] Determined by the collecting-index method of Taggart, Taylor and Ince: *Ante.*

reactions between the reagents and compounds occurring at the surfaces of the particles affected. Evidence, thought to be conclusive, is offered in support of this hypothesis.

2. Considerable detailed experimental evidence of the nature of the chemical reactions between particle surfaces and flotation reagents is given.

3. Evidence is presented tending to disprove the classical explanation of Brownian movement.

4. An alternative hypothesis of the mechanism of Brownian movement is set forth, and evidence in support thereof adduced.

5. Complete correlation between Brownian movement and the collection phenomena in differential flotation of lead-zinc-iron-silica is shown.

6. The use of Brownian movement and the new hypothesis as a powerful tool in the investigation of flotation phenomena is demonstrated.

### Acknowledgments

Grateful acknowledgment is hereby made to G. R. M. del Giudice, lecturer in mining; T. Cleon Fitt, Trowbridge Fellow in engineering; and Othon Ziehl, J. C. Munday and F. X. Tartaron, research assistants in ore dressing and in chemistry, all of Columbia University, for faithful and enthusiastic assistance in the experimental work described in the present paper.

## DISCUSSION

O. C. Ralston, Clarkdale, Ariz. (written discussion).—This is an important paper and the authors are to be congratulated on their development of methods that permit collection of definite experimental evidence to support a chemical reaction theory of flotation collectors, modifiers and activators. The theory is not new, as sulfide filming was practiced commercially over 15 years ago, even in the dark ages of "oil" flotation. The use of copper sulfate as a flotation activator since 1911 has also caused certain minds to carry a chemical reaction theory, but the definite experimental support for chemical reactions as modifiers of mineral surfaces has been meager.

The chemical theory has always attracted me but I still lack the courage of the authors when they state in conclusion 1 of this paper that "in flotation with soluble reagents, *all* phenomena governing collection are controlled through simple chemical reactions . . . " This is a great change from Professor Taggart's former absorbing interest in adsorption. Such sweeping generalizations are always dangerous and almost invariably subject to limitation or modification. Let us not be swept away by these enthusiasts, no matter how acceptable their data may be.

We are still faced by the fact that some mineral particles are water-avid, others air-avid, and that by properly modifying them they may be enhanced or diminished in desirable or undesirable avidity. Coatings on minerals must still be assumed to fall into three classes:

1. A coating of immiscible oil.
2. A layer of adsorbed substance.
3. A chemically produced coating.

The older style oil flotation methods, until shown to act otherwise, probably did actually oil or grease the surfaces of certain mineral particles because of certain balances of interfacial tensions which favored selective greasing. However, these oils were not soluble and we must observe that Taggart et al. restrict themselves in their generalization to *soluble collecting reagents*. Frothing agents are not under discussion, nor insoluble collectors.

With regard to layers or coatings obtained through adsorption, I believe the conclusion justified that *most* soluble collectors function mainly through chemical reaction and cases of adsorption only will be hard to find. Until all soluble collectors have been shown to function by chemical reaction, the generalization of Taggart is unsafe. Below, in discussing Brownian motion, will be found reasons why I feel Taggart does not entirely escape adsorption.

I notice on page 220 the statement that Gates and Jacobsen were the first to publish evidence of chemical reaction between reagent and mineral particle under modern flotation conditions, having worked on the reaction between copper sulfate solution and sphalerite. This reaction is not modern. Copper sulfate solution is acid in reaction and acid flotation circuits are now extremely rare. The reaction of copper on sphalerite was studied by myself and coworkers[63] under modern conditions; *i. e.*, alkaline circuit. The copper sulfate was fed into a lime solution and the effective copper compound was shown to be the copper hydrate—not the sulfate. We also showed the chemical formation of a film of cupric sulfide on the sphalerite under these conditions. Our work was not antedated by anyone else. Even Emmons' exhaustive discussion of mineralogical chemistry, of which Taggart quotes five pages, does not antedate our work with copper hydrate. The Emmons compilation on mineralogical chemistry and the F. W. Clark volume on Data of Geochemistry have been suggestive sources of information to most flotation workers, but it is well to point out that the time intervals used in most of this geochemical research have been great in comparison with the time for reactions of importance to flotation. How can one feel safe in assuming that a reaction, reported by a geologist as having been allowed 72 hr. to produce a certain result, will take place in the 1 to 30-min. interval common to flotation work? Therefore, the exclusion of our papers from Taggart's review is regrettable.

The fancied correlation between Brownian movement of mineral particles and their suitability for flotation is an instance of fallacious reasoning. We can restate in different words the finding of the paper: that particles possessing Brownian movement are *not* in condition for successful flotation. This may be true but one could also point to scores of other physical properties which if possessed by mineral particles unfit them for flotation. Inverse correlations are useful but should be displaced by use of their reciprocal of direct correlations. Let us seek the direct correlation in this case. Particles displaying the Brownian movement have sufficient density of electric charge to be deflocculated, and on changing the electrolyte in contact with them in such a manner that the density of charge is sufficiently decreased, flocculation sets in, as pointed out by Taggart et al. Then flotation becomes easy. The correlation of flocculation with successful flotation concentration of the floatable minerals is probably 15 years old. One of the best mechanical and physical explanations of one way in which flocculation assists flotation was presented in an unnoticed and nearly

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[63] O. C. Ralston, C. R. King and F. X. Tartaron: Copper Sulfate as Flotation Activator for Sphalerite. See page 389.

O. C. Ralston and W. C. Hunter: Activation of Sphalerite for Flotation. See page 401.

forgotten paper by Coghill and Anderson[64] discussing the "edge effect." We therefore find in this "new" Brownian motion correlation nothing but the old "necessity of flocculation" togged out in a new dress. The situation would be the same if I insisted that one needs light in order to see and Taggart discovered that one needs dark in order not to see.

Not content with the "necessity of absence of Brownian motion" we find that the authors of this paper have an alleged new hypothesis to explain Brownian motion in contrast with what is called the classical theory. The statement of just what is the classical theory is not clear, so it might be well to amplify it here.

The classical theory is based on the kinetic theory of solutions. In accordance with kinetic theory, the molecules and ions in a solution are in continuous movement and frequent collision with each other and the walls of the containing vessel. A suspended mineral particle is bombarded on all sides by these ultimate molecular or atomic particles but the average number of impacts at any instant on one side will be exactly balanced by an equal number on the other side of the particle. For very small particles the area to be bombarded becomes relatively small and collisions fewer in number, until we might find an instant when say 1000 molecules or ions collide with a particle from below and 1001 of them collide with it from above. The result will be an impulse in the downward direction. The next instant the particle may be knocked in the reverse direction or to one side. This is Brownian movement. It is possessed by only very small particles of "colloidal" dimensions. Parenthetically, it is not discernable on 95 per cent. or more of the solids in a flotation pulp because of their relatively large size. It is immaterial to the kinetic theory whether the bombarding corpuscles are electrons, ions, molecules or aggregates of molecules. Kinetic theory of solutions is based on such overwhelming evidence that it forms an acceptable basis for explaining any physical phenomenon and when an attempt is made to ignore kinetic theory or discredit it, the result is usually disastrous. So much for the case of motion of the mineral particles. Let us now discuss the electric charges on them.

The usual suspended particles of matter will be electrically charged. Bombarding ions from the solution might rebound from the particle surface or might stick to it, temporarily at least. Some of the best accepted colloid theory assumes that ions of both electric signs and molecules do stick for at least a limited period of time on surfaces, and the condition is called "adsorption." A large body of evidence proving adsorption has been built up. The reason for adsorption is based, according to Langmuir,[65] in the electromagnetic field of force that surrounds each of the atoms forming the surface of the suspended particle. These unbalanced fields of force hold molecules or ions that strike at favorable points in a favorable manner. Later the bound masses leave or are knocked off again. Some of the surface atoms of the mineral particle itself may pass off as ions. If an excess of positive ions over negative ions is held on the surface, the particle will have a positive or a negative charge. Rarely does it happen that a surface will have the property of attracting or retaining oppositely charged ions in exactly the same quantities. Also, different ions of the same sign will be adsorbed in varying amounts, as one would expect a difference kinetically between the behavior of a heavy lead ion and a light hydrogen ion. Therefore every soluble substance added to the solution in which particles are suspended will impose a new ionic condition on the solution and a new balance will be struck in the proportion of ions which are adsorbed. If the new balance can be made so that an excess of neither positive nor negative ions is held in the adsorbed layer, the particle is electrically

[64] W. H. Coghill and C. O. Anderson: Certain Interfacial Tension Equilibria Important in Flotation. U. S. Bur. Mines *Tech. Paper* 262 (1923).

[65] I. Langmuir: The Constitution of Liquids with Especial Reference to Surface Tension Phenomena. *Met. & Chem. Eng.* (1916) **15,** 468.

neutral and is spoken of as being at its "isoelectric point." The particles now no longer repel each other, as explained by Taggart, and can gather into floccules through the forces of interfacial tension, because there is the opportunity for a decrease in total surface energy. It is floccules which are easily floated. Why one should wish to abandon flocculation with its positive correlation to good flotation and study Brownian motion, which is concomitant with deflocculation, is difficult to understand. Figuratively speaking, in one we look at the doughnut and in the other we look at the hole in the doughnut.

Let us now examine Professor Taggart's new picture of the causes of Brownian movement. (1) The "bombardment" or collision theory must be abandoned. (2) The unbalanced adsorption of ions from the solution must be abandoned. (3) All one needs to do is to assume that the mineral particles themselves ionize or lose ions into the solution and that motion of the particle is due to unbalanced vibration between the ionized and the unionized states. That is as clear as the authors make it. We must add a few implications. A suspended particle of sphalerite might lose a zinc ion to the solution, and this zinc ion will be positively charged, leaving the remainder of the sphalerite particle negatively charged. (The same is possible by the classical theory.) Taggart insists that the motion of the mineral particle is due solely to the departure or return of ions generated from the particle itself. He thus uses kinetic theory as far as the ions are concerned but excludes arrival or departure of molecules as being effective. Also, if an ion collided with the particle surface but rebounded, Taggart would have to say its action was ineffective even though no other ion collided simultaneously with the opposite side of the particle. Only when that free-moving ion strikes the particle surface and is captured or remains, thereby changing the condition of ionization on the particle, has an effective kick been given to the mineral particle so that it moves. Also, let us picture the departure of the first zinc ion from the surface of a sphalerite particle freshly suspended in a suitable liquid. Its departure seems to cause a back kick or recoil, if we properly interpret Taggart's viewpoint. This is a sort of explosive ionization; improbable, yet it is necessary to the theory.

Both the classical theory and the Taggart hypothesis leave the particle electrically charged but whereas the classical theory has electric charge due to preponderance of ions of one electric charge, whether from the solution or the particle itself, Taggart says the charge comes solely from ionization of the particle itself. Thereby he escapes having to assume any adsorption of ions on the particle surface. Apparently adsorption is now a hideous thought.

The new hypothesis cannot escape use of the kinetic theory of matter but has to make the artificial restriction to kinetics of ions only and is forced to assume an explosive kind of ionization. As there seems to be a total lack of evidence to support this hypothesis it is probably best to leave to the physicists and physical chemists the problem of justifying it.

The recorded behavior of different mineral particles in various solutions under the microscope may be accepted without its having to constitute proof of the new hypothesis nor need the new hypothesis be invoked in order to explain the observed phenomena. In the case of galena, if lead is the "anchored" ion, either theory explains how it came to be so. The solubility of the substances making up the particles and its effect on Brownian movement is of as much importance to one theory as to the other. Too soluble a substance supplies too many ions of both kinds to the solution immediately contiguous, so that it is hard to get a sufficiently dilute solution to allow an unequal number of moving ions or molecules to impinge on or leave opposite sides of a small particle at a given instant and thus cause its movement.

In connection with the hypothesis of a correlation between a certain range of solubility and Brownian motion of a particle of substance, it would be interesting

to ask the authors to explain the Brownian motion of a particle of colloidal gold in distilled water. Here is a substance of extremely minute solubility; hence a very small number of gold ions leaving at any instant in comparison with the hailstorm of hydrogen and hydroxyl ions from the water which impinge on the particle surfaces. Furthermore, according to the Taggart hypothesis, only gold ions could form and diffuse away, leaving the particles of gold invariably negatively charged. How then is it possible to explain sols of gold where the particles are positively charged?

Lastly, if flocculation of the floatable mineral is the important condition, why not study flocculation with the low-power microscope or the unaided eye instead of having to go to the trouble of studying Brownian motion by the help of the ultramicroscope and special expensive illuminating apparatus?

L. F. Clark, Gard, France (written discussion).—I have followed Professor Taggart's work with great interest and appreciation. The general trend of his observations seems to point to chemical exchange reaction at mineral surfaces as the mechanism whereby collectors are attached thereto. It would seem also from his work that this attachment reaction takes place best on sulfide surfaces which are not entirely pure but which rather have been preliminarily filmed by oxidation—in other words, that the attachment reaction takes place best on oxide surfaces. He believes this is further verified by the more extensive and even visible attachment which takes place on oxide mineral surfaces as compared with sulfide surfaces. But this type of attachment does not lead to good collection, or oxides would float better than sulfides; nor does it explain the attachment of trivalent nitrogen compounds, as Professor Taggart himself has pointed out.

I cannot therefore yet agree that direct chemical exchange reaction is the true explanation of attachment of collectors to minerals in so far as such attachment leads to collection and recovery by flotation. Fully admitting that this type of attachment does often take place, I regard it as actually detrimental to good collection and a mere wasteful consumer of reagent. The type of attachment that leads to collection is something different. It is a union of peculiarly bound valence bonds at the mineral surface and in the reagent, probably without actually disrupting the already existing structures. Possession of such peculiarly free valences makes a reagent function as a collector, and it makes a mineral "collectable." The "collectors" and the "collectees" are strangely alike in some respects. On the side of the minerals, it would seem that this property is characteristic of atoms of elements or simple molecules formed of any elements except oxygen and the halogens; *e.g.*, metal arsenides, carbides, hydrides and sulfides.

The attachment of collectors on to oxide mineral surfaces, which leads to good flotation recovery, must be brought about by preliminarily modifying these surfaces into compounds such as are mentioned above. The reagent collectors can then adhere in the proper type of attachment. This form of preliminary coating however is ineffective on silicates where a silica skeleton probably persists as the outermost shell. Nor does formation of soaps on oxide mineral surfaces make a suitable base for "collector" attachment.

It seems to me that Professor Taggart is on the right trail toward correct elucidaion of these phenomena but that the readily available explanation of exchange reaction leads away from the truth. I shall continue to follow his work with keen attention.

A. W. Fahrenwald, Moscow, Idaho.—What was the size of grains used in your Brownian movement experiments?

A. F. Taggart.—About 2 to 15–30 micron. We work at about 2500 to 3000 diameters.

A. W. Fahrenwald.—Is the Brownian movement significant in flotation, or does it just happen to be a coincidence that when there is reasonable solubility there is Brownian movement, and that when there is nearly complete insolubility there is no Brownian movement? Does Brownian movement have anything to do with flotation or with our present generally accepted theories of flotation?

A. F. Taggart.—I failed to say in my presentation that we believe that Brownian movement will only occur when the surface is soluble somewhere to the extent of 1 to 30 mg. per liter, and is ionized with one of the ions anchored to the surface of the particle. If the surface is soluble and ionized, that means that it is water-avid and consequently bubbles will not stick to it. Thus Brownian movement is a definite indicator of surface wetting. That is the reason that particles in Brownian movement will not float. The surface must be closed up, as it were, and ionization must be stopped, before there is any possibility of the surface being water-repellent. Even after the surface is closed up, it is not necessarily true that the particle will float, because unless the closure has been effected by means of an ion that is water-repellent, the hydrocarbon ions from organic flotation agents, for instance, the surface has been rendered merely insoluble, not water-repellent. If, however, it has been closed with such a hydrocarbon ion, it will float. There may be, however, failure to float without Brownian movement, indicating, of course, that the surface is more soluble than will give Brownian movement.

A. W. Fahrenwald.—Then Brownian movement is an indicator of whether a grain possibly will float or will not float?

A. F. Taggart.—It is an indicator that it will not float.

A. W. Fahrenwald.—Conversely, then, substances that are non-wettable do flocculate.

A. F. Taggart.—Yes, they will flocculate, but other substances will flocculate: that is, they need not be non-wettable in order to flocculate.

A. W. Fahrenwald.—Professor Gaudin, of the School of Mines at Butte, Montana, says that sphalerite in clean water is not floated by xanthates.[66] Presumably the whole explanation is that zinc xanthate is too soluble. How does this fit into your movement and solubility theories?

A. F. Taggart.—If the surface solubility exceeds somewhere between 30 and 40 mg. per liter, there is no Brownian movement.

F. G. Breyer, New York, N. Y.—When you say that the solubility goes so many grams per liter, do you mean that that is the solubility reported in the textbooks?

A. F. Taggart.—In some cases it is and in some cases it is not, in these that I have given.

F. G. Breyer.—Have you not found that the total amount of material in solution in the water depends on the amount of surface exposed as a consequence of crushing?

A. F. Taggart.—You are getting into something that I do not know much about The solubilities that I have been talking of are solubilities that are determined when we take the substance itself and attempt to get it into solution by any one of a variety of means, but I do not know whether the solubility of lead xanthate at the surface of a lead sulfide particle is the same as the solubility of lead xanthate prepared independently and then put into the water.

The figure that I have given for solubility of the lead xanthate is, of course, based on a determination of the solubility of lead xanthate independently prepared.

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[66] See page 417.

We do not know the solubility of lead xanthate when the lead is anchored on lead sulfide. We are rather inclined to think that in every case the solubility of the substance as a surface coating is somewhat less than that of the same substance independently put into solution, but I do not know.

F. G. Breyer.—It would seem from observations of very large surfaces in other mediums than water, mostly in oils, that the particular figure that is significant is the solubility of the material per unit of surface exposed. There is good evidence that the total amount of soluble material is a direct function of the amount of surface exposed. For example, a silicate mineral which has a reported low solubility in water will show a great increase in alkalinity of a slurry made from it when more finely ground. The finer the grinding, the higher the pH of the slurry up to a certain point.

A. F. Taggart.—Very true. We have become suspicious of all the published solubility figures.

F. G. Breyer.—When you have reduced a material to below 10 microns, the published solubilities have no significance whatever. They have all been made with much less surface exposed to solution by the suspending medium.

A. F. Taggart.—If our theory of the Brownian movement is correct—that it is due to an ionized surface—then our observations are confirmation of that statement. When we put silica into distilled water under a microscope the particles are immediately in motion. We prepared silica by taking quartz as pure as we could get, soaking if for several days in a chrome-acid cleaning solution, then washing it in running tap water for a term that ran into weeks instead of days, then in distilled water, then grinding it in a porcelain mill and then igniting it in a muffle just short of the fusing temperature. It was free of at least the bulk of outside substances and yet that stuff was in vigorous motion; also, the solution that it was in had a pH above that of ordinary water. We think what happened there was that the glass of the side and cover went into solution to give a sodium silicate.

F. G. Breyer.—Is this answer to Professor Fahrenwald's question reasonable? Assuming that the several minerals have been mechanically broken one from another, the first thing sought is a dispersing means that will put all the particles in active Brownian movement. This movement will keep them separated one from another. Then a flocculating agent is sought, which will flocculate the minerals only and will flocculate the bubbles of air with the mineral flocculate, so that the whole business will go up to the top.

A. F. Taggart.—That is about what we get by our collecting agent, although I do not think that flocculation is at all an essential; I think it is merely an indicator. As soon as you stop the Brownian movement by rendering the surface too insoluble for Brownian movement, that means that there is no longer an ionized surface; particles no longer are charged electrically therefore. Hence there is no longer any tendency for them to keep apart. Watching them under the microscope we see that there is no tendency for them to pull together at all; whenever a couple of them bump together, they stick, but apparently it is a mechanical bumping that brings them together.

A. W. Fahrenwald.—What would you expect to find in the way of Brownian movement of pulverized quartz in hydrofluoric acid solution where the solubility is considerably greater than quartz in water?

A. F. Taggart.—What is the solubility of the surface, do you know?

A. W. Fahrenwald.—No, I do not, but it is much greater.

A. F. Taggart.—Our experience is that if it exceeds between 30 and 40 mg. per liter, there is no Brownian movement. We have been working with other things that have nothing to do with flotation, and usually we can put the particles into Brownian movement if we can get the surface within that solubility.

F. G. Breyer.—Am I correct in saying that unless the flocculating tendency is sufficient to keep the particles together when they are mechanically brought in contact the air bubbles will not attach to the flocculates?

A. F. Taggart.—I think that would follow, but not by reason of any connection with the flocculating tendency. If the particles are to stick to air bubbles, they must be coated with an organic compound which has a water-repellent hydrocarbon end, and if they are going to be thus coated, the surface is likely to be soluble to an extent of less than 1 mg. per liter. Under those circumstances, flocculation will occur. I do not think that it works the other way; that you coat and flocculate and then float because of the flocculation. You can float because of the insoluble water-repellent coating, and you can flocculate because of the insoluble water-repellent coating, but they are independent phenomena.

F. G. Breyer.—I was thinking of an analogy. A dry pigment, for example, without any differently ended molecules stuck on the surface of the particles is flocculated. If there is no dispersing agent in the water in which it is suspended the air bubbles within that flocculate will float it.

A. F. Taggart.—But they are there from the beginning.

F. G. Breyer.—It is analogous. A flocculate of very heavy dense zinc oxide particles, for example, with a specific gravity of 5.5, will float because of the air bubble or pocket within. That is my picture.

A. F. Taggart.—You started from a different place there. You put an already finely ground dry pigment into oil or into water. We put a coarse mineral into water and subdivide it under water and subsequently attach the air to it, which is quite a different thing. You cannot attach the air to it if it is of the same nature as the pigment without the liquid-repellent molecules.

W. L. Zeigler, Wallace, Idaho.—It seems reasonable to suppose from hearing Professor Taggart that the finer the particles are ground, the more active the chemical action will be on the surface, yet in actual practice we find that when the minerals are ground extremely fine, we lose flotation; and I think that we can prove by tests that overgrinding—grinding for an extreme length of time—will absolutely ruin flotation. In actual practice we have that condition with the natural slimes. I cannot exactly correlate the chemical action into the action we get in practice. I would like to ask Professor Taggart if he has anything on the subject.

A. F. Taggart.—I do not think that it follows that chemical reaction per unit of surface varies at all with the fineness of grinding. The aggregate of chemical reaction, of course, if that reaction is with a surface compound, will increase with the increased surface. I do not know the answer to the question of overgrinding. I have an idea, however, particularly when you tie it up with the primary slimes. It goes back to some work that we did several years ago on the slime coatings at sulfide mineral surfaces. This, for instance, is an experimental fact: that galena in a distilled-water suspension of quartz is not coated with quartz but that the addition of a small amount of lime to the solution will cause the galena to be coated with a firmly adherent layer of quartz particles of such a thickness and effect that an air bubble will not stick to galena particles in the presence of a collecting agent. On the other hand, a galena particle in a distilled-water suspension of slime from a run-of-mine ore from Anaconda is coated similarly with the slime particle so that a bubble will not adhere to the

surface in the presence of a collecting agent; while if to that mixture the same amount of lime is added as in the preceding case, the surface is free of slime and flotation can be readily effected.

That is substantially as far as my experimental knowledge on the subject goes. I do know that, in general, when the surfaces of the sulfide particles are slime-coated there is poor flotation, and that a reagent that affects and lessens the slime coating generally aids flotation.

I have a suspicion that if you will keep the primary slime out, you can grind the mineral as fine as you want to and still float it. Gaudin's experiments with pure minerals at Utah would seem to indicate that, because he ground and classified so that he was working between 200 and what he calls 600 mesh and he got satisfactory flotation.

W. L. Zeigler.—In mechanical grinding, it is a question whether we can grind such particles so fine.

A. F. Taggart.—It may be that overgrinding merely means that a sufficient length of time has been given to get a thorough and complete slime coating on the sulfide particles and also to use up completely by reaction with the various constituents in the ore the particular reagent that has been put in to prevent the slime coating, and that will for a short time prevent it.

W. L. Zeigler.—We can take the slime and have that difficulty with it or overgrind the material and still get the same condition.

A. W. Fahrenwald.—I think probably Professor Taggart's guess is correct, that if the primary slime is removed there will not be any flotation difficulties from overgrinding. We have made a number of grinding and flotation tests on a lead-zinc ore, the time of grinding being the variable. The metallurgical results of all the tests were equally good.

R. W. Lawrence, Kenvil, N. J. (written discussion).—This paper, particularly the ingenious hypothesis for the Brownian movement, interested me considerably. It seems to me, however, that the authors in proposing their hypothesis have neglected a study of the rather voluminous literature on the Brownian movement. Furthermore, one cannot help feeling that the data adduced in support of their theory are somewhat conflicting and support the kinetic theory of Brownian movement rather than that of the present authors, and beyond this there is a certain weakness in the theory they propose.

It was shown by Jevons[67] that the addition of small quantities of an electrolyte caused the disappearance of the Brownian movement in certain cases investigated. However, Svedberg found that by taking sufficiently dilute suspensions in which the collisions between particles were infrequent the Brownian movement was not affected by the addition of electrolyte.[68] This experiment shows that cessation of the Brownian movement is caused by flocculation of the particles and that when the suspension is sufficiently dilute the particles do not collide often enough to permit of agglomeration and therefore the phenomenon is not affected. From this it appears that it is essential to show conclusively that flocculation cannot or does not take place before it can be shown that the electrolyte has any direct effect on the Brownian movement.

The experiments which have been brought forward in support of the proposed hypothesis are as well or better explained by the old kinetic theory of the phenomenon.

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[67] W. S. Jevons: On the So-called Molecular Movements of Microscopic Particles. *Proc.* Phil. Soc. of Manch. (1869) **9**, 78.

[68] Nova Asta Regiae Soc. Scient. Upsala (4) 2, No.1, 146-155.

From the experiment on page 240 it cannot be said that an individual particle of such and such size, which was not altered during the experiment, ceased the Brownian movement in sulfuric acid and commenced it in sodium carbonate solution. On the other hand, the particles behaved just as they should have on the classical theory. "They first slowed down"—due to adsorption of very small particles by larger ones through collisions—"seemed to settle"—because of their increased mass—"strike bottom . . . , but eventually each settled down and stopped." It seems very likely that the larger particles might grow rapidly by accretion of smaller, perhaps unresolvable particles. This would account for a slowing down and eventual stopping of the movement.

On page 241 it is stated that flocculation occurred in acidified water and that the floccules were dispersed or partly so in sodium carbonate solution. This, of course, supports the classical theory. It simply shows that the material flocculates in dilute sulfuric acid and disperses in dilute sodium carbonate solution. Hence, sufficiently large particles do not show the Brownian movement and settle out of solution while small dispersed particles show the phenomenon in accord with the kinetic theory of the Brownian movement. On page 244 it is stated that galena, sphalerite and pyrite were flocculated and motionless in distilled water but were dispersed and in movement in sodium carbonate solution. Again the large flocculated particles are too big to be in movement while the small dispersed ones are in movement. No action of the electrolyte other than that of dispersing agent is required to account for this behavior.

It is stated that "the suspension of the visible particle is due to the mean pull on it of the surrounding swarm of free-swimming ions, which are in turn maintained dispersed by whatever forces induce ionic solution." It is difficult to understand why the mean pull of these free-swimming particles should be any more likely to draw the particle into the solution than out of it or why the mean pull should not be zero. It is also doubtful that any momentary unbalanced electric field caused by the ions would be great enough to have any effect on any particle as large as these under discussion (say of the order of 1 or 2 $\mu$ in diameter) or sufficient effect to produce the Brownian movement. Nor can this theory explain the results obtained by Perrin[69] on the distribution in a gravitational field of particles in suspension. He was able to show that at equilibrium the decrease in concentration of the particles from the bottom to the top of a solution varies in the same manner as the decrease in density of a gas with increasing height. He showed that the particles of a very dilute emulsion distribute themselves under the influence of gravity in the same numerical fashion as do the molecules of a gas or of a dissolved substance; and that therefore the Brownian movement corresponds entirely to the molecular movement required by the kinetic theory.

It is very probable that the kinetic theory of Brownian movement can be adapted as readily to the study of flotation processes as that proposed in the paper. It is very likely that a study of Brownian movement will enable a determination of the proper conditions to produce a particle size which will permit of flotation.

T. J. Hoover, Stanford University, Calif. (written discussion).—This paper is a valuable contribution to applied science. For the purpose of completeness in the references to the work of predecessors, there should be added the work of Lieutenant G. J. Frost in 1914, account of which is given on pages 283–287 of Concentrating Ores by Flotation, 3d Ed., *The Mining Magazine*, London, 1916.

A. F. Taggart, T. C. Taylor, A. F. Knoll (written discussion).—It is flattering to authors for their work to arouse such interest as is evidenced by the heat of Mr.

[69] J. Perrin: Mouvement Brownien et Réalité Moléculaire. *Ann. de Chim. et de Phys.* [8] (1909) **18**, 5.

Ralston's discussion. And were Mr. Ralston's warmth a reliable indicator of the acuity of his study, the authors would welcome the discussion as clarification of their efforts at exposition and confine their reply to simple thanks. But unfortunately this is not the fact. Mr. Ralston's contribution contains so much that needs correction and elucidation that, since we provoked the storm, we must assume the burden of clearing up a part, at least, of the debris.

First, the more obvious things. We state no "Conclusion 1," but in paragraph 1 at page 246 under the heading "Summary," postulate an idea which is carefully and specifically labeled hypothesis. We think the evidence adduced convincing. We even think enough of the hypothesis, on the data so far unearthed, to print it in italics on page 219. If that is courage, as Mr. Ralston so defines, we confess to it; if foolhardiness, we stick to it. But in neither case do we dignify the idea beyond what is implied in the designation "hypothesis."

Inconsistency of attitude on the subject of adsorption in flotation is attributed to one of the authors. We do not exactly know the purpose of this part of our critic's outpouring. If he sets it forth as discovery, it seems to us an indication of not too acute reading on his part. Because our paper, on the first page, calls attention to this very change. We are no longer willing, as our critic seems to be, to adopt the ostrich attitude of thinking that because we name a certain set of observed phenomena adsorption, we have thereby explained them. We may yet in the future, in moments of forgetfulness, use the word in the restricted sense of our modified definition. But when we can talk in terms of greater knowledge, as we are able to do with respect to the abstraction of dissolved collecting agents by sulfide mineral particles, we shall do so.

Mr. Ralston states: " . . . some mineral particles are water-avid, others air-avid . . . " The context indicates that he refers to the minerals as they occur in nature, uncontaminated and unmodified by handling. The profession should be indebted to anyone who can show this conclusively. Experiments have been carried out over the past 15 years in the laboratory of one of the authors seeking to demonstrate the truth of this subject. With the knowledge thus acquired we lack our critic's courage. What we know is that whenever we have produced a surface of metallic luster which we were sure was uncontaminated by organic matter, that surface was just as water-avid as a clean quartz surface. On the basis of experience we would replace Mr. Ralston's dogmatic assumption with the postulate that some mineral particles become contaminated with organic matter—oil from rock drills, crushers and the like—with amazing ease, and thereafter display distinct water repellence, while other minerals are not readily so contaminated and are correspondingly easily water-wetted.

Mr. Ralston falls into an error in reading, and likewise, apparently, into one of fact, when he discusses priority in connection with copper sulfate and sphalerite. Our paper does not state that Gates and Jacobsen were, but that they "*seem* to have been the first to publish evidence of chemical reaction between reagent and mineral particle under modern flotation conditions." (Italics ours.) It goes on to tie this work in to copper sulfate and sphalerite. So much for the way the statement was made. We stick to it in the face of our critic's evidence. His cited prior publications are dated 1929; the Gates and Jacobsen article was printed in 1925.

If Mr. Ralston is making the point that the reaction of copper sulfate with the surface of sphalerite particles depends on first rendering the copper into hydrate, that is another matter. On that, as a fact, we should like further evidence. It has no bearing, however, on the matter at present under discussion.

As to our failure to include in our review the papers that Mr. Ralston cites, the omission was based on the facts presented in our footnote 53, which discussed part

of another paper on similar work, for which work and paper Mr. Ralston was, presumably, primarily responsible.

Mr. Ralston, scorning our correlation between Brownian movement and flotation, says that "one could also point to scores of other physical properties (than Brownian movement, presumably) which if possessed by mineral particles unfit them for flotation." We are irresistibly reminded of the little girl who would not eat her rice pudding. Her fond mamma urged upon her attention "scores of little girls who would love to have it." The youngster, from a fact-requiring heritage, retorted: "Name three." In this instance, we double for the little girl.

We turn next to the "correlation of flocculation with successful flotation concentration," which Mr. Ralston says "is probably 15 years old," and for adherence to which he pleads. If such correlation is merely the inverse of the correlation with Brownian movement which we have set up, and Mr. Ralston so asserts, well and good. It then serves as further corroboration of our observations. But there it stops. It and its proponent offer no explanation for the parallelism with flotation phenomena. We postulate that collection through the agency of dissolved reagents is due to simple chemical interchange; that Brownian movement is connected with the same or related chemical phenomena; and that the scientific basis of our correlation lies therein. We find nothing in Mr. Ralston's discussion to weaken our confidence in the rigor of the reasoning. We shall discuss his correlation more at length later.

We might, we think, question our critic's success in clarification of our statement of the classical theory of Brownian movement. We admit that he uses more words. But when he asserts as a fact that Brownian movement "is possessed by only very small particles of 'colloidal' dimensions" (the tautology is his) and "is not discernable on 95 per cent. or more of the solids in a flotation pulp because of their relatively large size," he leaves the realm of opinion and ventures, presumably, into the field of fact. Then we become interested. We should like to know what sizes he sets as covering the colloidal range. We have observed Brownian movement of sphalerite flocs 15 by 24 $\mu$ in the dimensions visible, which is considerably beyond what most investigators acquainted with the subject class as the upper size limit of the colloidal range. We think it logical to conclude that the chemical state of the surface of particles of a given substance larger than this is the same under the same conditions as that of the smaller particles of the same substance. Hence we do not see how it affects the question, even if it were true, that "95 per cent. or more of the solids in a flotation pulp" are too large to move. The state of their surfaces is the same as that of their smaller companions, and is indicated, within the limits set forth in the main paper, by the behavior of the smaller particles.

We are accused at one place in the discussion of "ignoring" the kinetic theory in our new hypothesis and warned of the danger of such neglect. Later we are told that "the new hypothesis cannot escape use of the kinetic theory . . . " It is too confusing. We would have to change sides as often as our critic to answer this

The paragraph in Mr. Ralston's discussion which paraphrases from an excerpt from Langmuir's classic paper on the Constitution of Solids and Liquids what the critic conceives to be what Langmuir said on adsorption is an example of the sins that are committed in that name. Langmuir, of course, had a clear idea of what he was writing about and used his words precisely. But the paraphrase starts by defining "adsorption" as a condition, instead of an act, which is not by any means Langmuir's use of the word. It then goes on to state as facts, or to attribute to Langmuir as statements of fact—it is impossible to tell which is the intent of the critic—a number of things which are purest postulate. Nobody would quarrel with the critic or with anyone else who thus qualified these statements and set them up as his credo. But as they stand they are misleading. For the sake of those who come to the subject more or less as beginners, we suggest that if such a reader will number the sentences

consecutively in Mr. Ralston's paragraph beginning: "The usual suspended particles . . . " (page 249), he should then read them as follows:

1. Most, if not all, discrete particles that will remain suspended more or less indefinitely in a fluid medium will migrate in an electric field. This indicates an electrical charge on such particles.

2. This sentence is already supposition. Certainly, if an ion did bombard such a particle it might stick or it might bounce off. It might also smash, or penetrate, or even, as the critic later postulates, explode. (We will take up this idea at another point.) It might, apparently, do anything that sweet fancy can encompass. However, there are no facts in this sentence, so let us pass on.

3. If anyone can make sense out of this sentence, let him test its truth himself. We have had to give it up. But whatever it means, it is not as well accepted as the critic implies in his characterization.

4. We question the word "proving" in this sentence. Substitute "of." Then use the definition of adsorption from page 217.

5. See the original Langmuir article. It is a classic.

6, 7. See whether Langmuir said these things as facts.

8. This, properly stated, we have given strong evidence for. Not that an atom passes off as an ion, but that the salts at the surface of the mineral particles ionize, one remaining anchored and thereby causing the particle to act as if charged, the other migrating into the solvent.

9. This, of course, is a part of our statement.

10. We agree with this whole-heartedly.

11. Apply our definition of adsorption.

12. We could all stand some evidence on this point.

13. This likewise. Mr. Ralston would do a service extending far beyond the art of flotation, if he could contribute something more than words here.

14. Modesty forbids comment.

15. This statement as it stands is not fact. Galena particles can be flocculated by adding a soluble chromate or dichromate. But the floccules cannot be thereafter floated with alkaline ethyl xanthate, or anything else, so far as we know. The new hypothesis explains this. Lead chromate and dichromate are substantially as slightly soluble as lead ethyl xanthate. The chromate coatings are not water-repellent and do not, therefore, effect collection. They are not replaced by an ethyl xanthate or similar coatings. Hence flotation of such floccules is impossible.

16. Comment 15 only partly answers this rhetorical question. Further, so far as the authors are concerned, they prefer a correlation which appears to have a basis in familiar chemical phenomena.

17. We'll take the hole—we can see further through it.

We should like to make it clear that "explosive ionization," which Mr. Ralston postulates on page 250, is his own conception—at least so far as we know. As such, it holds a unique position in his discussion.

Mr. Ralston asks us to explain the motion of a particle of colloidal gold in distilled water. We are more or less familiar with what is probably one of the most extensive researches on colloidal metals that has been made. Specifically with respect to gold, it cannot be suspended as a colloid in *distilled* water by any means now known. Beans and Eastlack[70] published a summary of their work on this subject showing that finely divided gold produced by arcing under water (Bredig method) could only be made to remain dispersed, *i. e.*, to assume the colloidal state when the water contained an electrolyte of which one of the ions was one with which the gold could unite

[70] H. T. Beans and H. E. Eastlack: The Electrical Synthesis of Colloids. *Jnl.* Amer. Chem. Soc. (1915) **37**, 2667.

chemically, *e. g.*, chloride or bromide. Nitrate, sulfate, etc. were ineffective. So we cannot explain the particular thing that Mr. Ralston asks about, because, so far as we know, it does not exist.

But colloidal gold suspensions formed by arcing in a dilute solution of potassium chloride, for example, are explained under our hypothesis as gold particles with a coating of potassium chlor-aurate, ionized to an unknown extent, the negative chlor-aurate ion being the anchored ion. The experimental fact that such a suspension is thrown down by an excess of potassium chloride is explicable, under the mass-action law, on the ground that the excess of the common ion, potassium, forces back ionization of the chlor-aurate until the number of ionized molecules on the surface of a given gold particle is so small that there are not enough free-swimming units attracted to a given particle to hold it up, nor a strong enough negative charge to repel other gold particles that approach.

We would ask that this explanation be substituted, in this connection, for Mr. Ralston's incorrect application of our hypothesis to the problem.

It is regrettable that we must answer to Mr. Ralston's query about positive gold sol the same thing that we answered as to negative sols in distilled water—we do not know of any. We presume, however, that he refers to the sol reported to have been made by chemical precipitation in the presence of an aluminum salt. This, like the negative gold sol, has been investigated thoroughly, and it has not been shown that it was anything else than aluminum hydroxide sol with gold mixed with the aluminum precipitate.

There is nothing theoretically difficult, however, in the idea of a positive gold sol. All that is necessary is to find a simple salt of gold whose solubility falls within the range of 1 to 30 mg. per liter and which ionizes in solution. Then form this salt on the surface of very fine particles of metallic gold. Our experience with a considerable number of suspensions points that under such conditions the gold particles would migrate to the negative pole in an electrical field.

As to Mr. Ralston's concluding rhetorical question, we answer: If the assumption therein is correct, why not? But we search Mr. Ralston's contribution in vain for one iota of evidence of such correctness. We are reasonably familiar with the field ourselves, and know of no such evidence.

Mr. Lawrence's attempt to correlate the facts of the experiment described on pages 239 and 240 with increase in mass of the particles overlooks the important fact that the fields examined, like the field pictured (Fig. 4), all contained particles of a size range of several diameters of the smallest particle resolvable. Hence any unresolvable increase in size of the smallest particle, such as Mr. Lawrence postulates, would still leave that particle of a mass far smaller than that of the largest particle in the field. And since the largest particle was in active motion prior to the addition of sulfuric acid, if the only change in respect of the smallest was one of mass, it should move in the presence of the acid. But it did not.

It is freely admitted that the proposed hypothesis has not been applied to all of the various phenomena of colloids, and hence that such a one as the classical experiment of Perrin may be posed without present answer. But the fact, asserted in the paper, repeated in the preceding paragraph, and now reasserted, that particles in Brownian movement may be stopped by the addition to the suspension of minute amounts of electrolyte, without flocculation or visible change of mass, and started again by the further addition of a minute amount of another electrolyte, without deflocculation or visible change in mass, the amounts of electrolyte added in both cases being far below what will cause measurable change in the viscosity of the suspending fluid, casts almost conclusive doubt on the molecular-bombardment theory.

# A Study of Differential Flotation

By C. R. Ince,* New York, N. Y.

(New York Meeting, February, 1929)

The term "differential flotation" is used to denote a flotation operation in which separation is effected between two or more minerals of the same class; *e. g.*, lead sulfide from zinc sulfide, pyrite from blende, chalcopyrite from pyrite, chalcopyrite from blende.

At present, so far as published work shows, there seem to be two theories as to the mechanics of differential flotation. The earlier and more generally accepted theory is that the so-called depressing agents alter the surface of one or more of the sulfides in the ore, either by chemical action or adsorption, so that it is no longer amenable to flotation, but that these depressed sulfides can be revived, after the unaffected sulfide has been floated, by reagents which react chemically with the altered surface and make it amenable to flotation. More recently, Professor Taggart[1] has advanced the theory that slime adsorption is an important factor in differential flotation. He believes that, with the proper use of a class of agents, which he calls dispersion agents and which include practically all the depressing agents, one can cause the slime to adsorb differentially on sulfide surfaces. A gangue-slime coated sulfide surface will act as a gangue particle and will not float. If, subsequently, an agent that will remove the gangue-slime coating is added, the sulfide again assumes its original surface and can be floated as an ordinary sulfide. This is the basis of the slime theory of differential flotation.

Timber Butte mill at Butte, Mont., is a typical lead-zinc flotation concentrator. Neihart ore, chosen for investigation in this work, is one of the custom ores treated at that mill. Practice at Timber Butte mill in February, 1928, was as follows: A combined lead-zinc concentrate was first made using 0.2 lb. per ton on the ore of potassium xanthate and 0.03 lb. per ton of Cleveland Cliffs oil after 1.5 lb. per ton of lime and 1 lb. per ton of calcium chloride has been added just before the ball mill. The concentrate was then thickened to 70 per cent. solids. Potassium cyanide to the amount of 0.3 lb. per ton and zinc sulfate in the quantity of 0.5 lb. per ton were added to the thickened pulp and the whole

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[1] A. F. Taggart: Handbook of Ore Dressing. New York and London, 1927. J. Wiley & Sons, Inc., and Chapman & Hall, Ltd.

heated to 140° F. in wooden tanks for a period of approximately ½ hr. After the conditioning period the pulp was diluted to 50 per cent. solids and treated, usually by pneumatic cells in which the lead sulfide was floated. The lead tails were then conditioned with 1 to 2 lb. per ton of lime and 1 lb. per ton of copper sulfate. A zinc float was made from this conditioned pulp using 0.2 lb. per ton of Barrett No. 4 and 1 lb. per ton of Aerofloat (25 per cent. $P_2S_5$).

Field practice seems to indicate that heating and time of conditioning are interchangeable. At Anaconda, in the zinc-lead concentrator, heating was dispensed with entirely but the length of time of conditioning averaged 3 hr. At International Smelting Co., Tooele, Utah, the lead-zinc concentrate was heated only to 80° F. and the time of conditioning varied from 1 to 1½ hr.

Professor Taggart defines dispersion agents as substances which, when added to an ore pulp, affect the state of dispersion of the gangue particles and at the same time change the extent to which these particles adsorb at sulfide-particle surfaces. Depressing agents, according to the same authority, are substances that are used to lessen the floatability of one or more of the minerals of the ordinary floatable class. It is apparent from these definitions that there will be members of the class of depressing agents that will fall under dispersion agents also. Those that hold to the slime theory of differential flotation therefore include alkaline cyanides, zinc sulfate and copper sulfate as dispersion agents as well as depressing agents. Conserving agents perform the function of protecting the other flotation agents from attack by substances present in the ore pulp—usually soluble salts.

According to this classification, lime is a dispersion agent. The writer has performed numerous tests which show conclusively that when added to an ore pulp it affects the state of dispersion of the gangue particles and also the extent to which they adsorb on sulfide-particle surfaces. Calcium chloride is a conserving agent. The fact that the amount of calcium chloride used at Timber Butte mill depended on the analysis of soluble salts in the mill water indicates this function. Potassium cyanide and zinc sulfate are depressing agents. The writer is inclined at this point to leave them strictly in that class and not include them under dispersion agents also. The evidence for this inclusion is too slender. The writer has never been able to cause the removal or adsorption of a slime on a sulfide-particle surface by the use of these reagents alone.

The following tests were performed in the course of the investigation. Their arrangement in series is to draw together for presentation the tests relating to the same phases of the work.

## Series I.—Gangue-slime Coatings

The procedure in all slime tests, unless otherwise noted, is that described under slime coatings in another paper presented at this meeting.[2]

Two particles apiece of galena and sphalerite were treated in a Neihart ore pulp consisting of 200 g. of freshly ground −65-mesh ore and 800 c.c. of distilled water. After 5 min. agitation, one particle of each sulfide was removed and prepared for examination under the microscope. Fig. 1 is a photomicrograph of the galena surface at 200 magnification. Fig. 2 is the sphalerite surface under the same magnification. Both slime coatings are distinct and fairly uniform in character. The sphalerite slime coating appears to be slightly heavier. At 480 magnification the

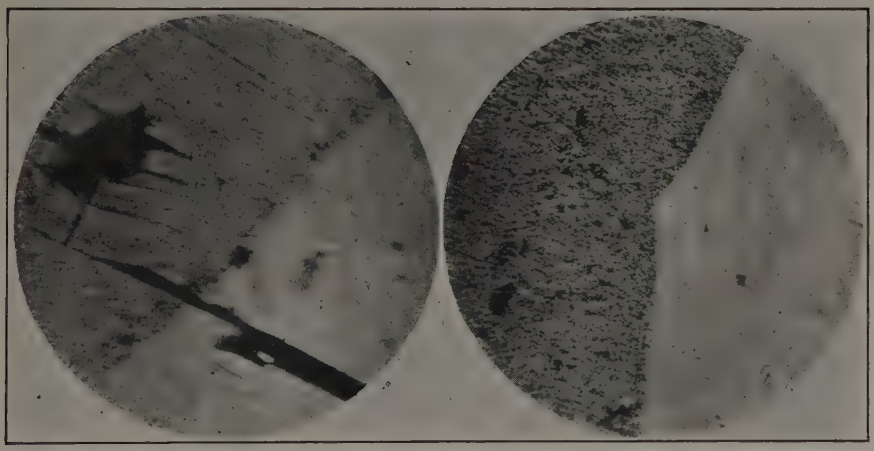

Fig. 1.—Neihart ore pulp, galena surface. × 200.

Fig. 2.—Neihart ore pulp, sphalerite surface. × 200.

slime coatings were found to be individual grains, irregular in shape and appearing brown by reflected light.

A sample of the slime was pipetted off and examined under the microscope. It was found to be dispersed (Fig. 3). A pH determination made on the pulp showed it to be 7.0 to 7.2, or substantially neutral.

Lime in the proportion of 1.5 lb. per ton in the ore was added and the pulp agitated for 5 min. The two remaining sulfide particles were removed and prepared for microscopic examination. The galena surface still revealed a slime coating similar in amount and character to that shown in Fig. 1. Actual count of slime particles on the surface by means of a "grid" ocular confirmed this observation. The sphalerite surface also showed a slime coating similar to that found in Fig. 2. However, an examination of a sample of the slime showed it to be distinctly floccu-

[2] A. F. Taggart, T. C. Taylor and C. R. Ince: Experiments with Flotation Reagents. See page 285.

lated, as shown by Fig. 4. The pH was found to be greater than 9.8+ strongly alkaline.

To the now alkaline pulp particles of galena and sphalerite prepared for slime-coating tests were added. After 5 min. agitation one particle of each sulfide was removed and examined. As shown by Figs. 5 and 6

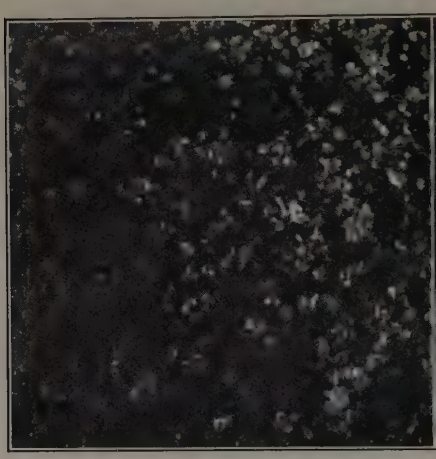

FIG. 3.—NEIHART ORE SLIME.

FIG. 4.—NEIHART ORE SLIME WITH LIME.

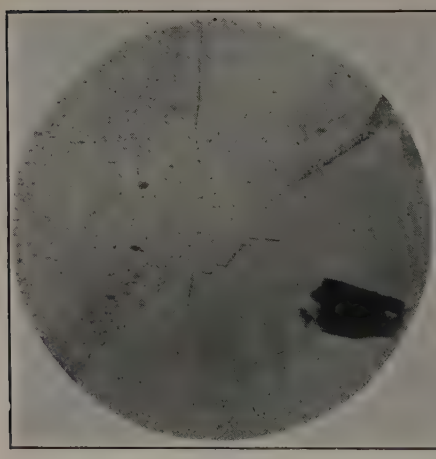

FIG. 5.—NEIHART ORE AND 1.5 LB. OF LIME, GALENA SURFACE.

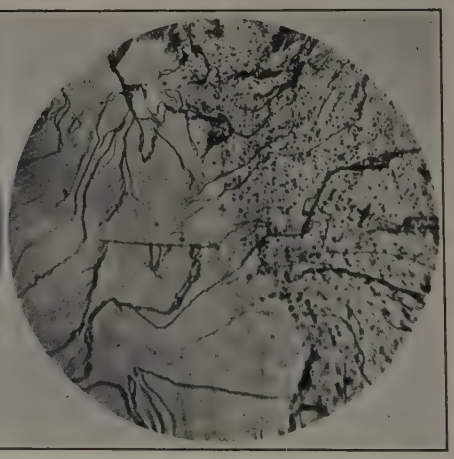

FIG. 6.—NEIHART ORE AND 1.5 LB. OF LIME, SPHALERITE SURFACE.

the slime coating was distinctly less than that obtained with the same pulp in the absence of lime (Figs. 1 and 2).

The pulp was then thickened to 70 per cent. solids, and 0.3 lb. per ton of potassium cyanide and 0.5 lb. per ton of zinc sulfate were added. It was conditioned at 140° F. for ½ hr. After dilution to 50 per cent.

solids and another 5-min. agitation, a particle of each sulfide was removed and a slime sample was taken. There was no change in the slime coatings on either sulfide, both revealing surfaces similar to those shown in Figs. 5 and 6. The slime revealed no change in state of dispersion, still remaining flocculated as in Fig. 4. A pH of 9.8+ showed the pulp to be distinctly alkaline.

Copper sulfate in the proportion of 1 lb. per ton in the ore and 1.5 lb. per ton of lime were added to the pulp. After a 10-min. conditioning and a 5-min. agitation period the remaining particles of sulfides were removed. Under the microscope the slime coatings were still found to be similar to those obtained after the first addition of lime to the Neihart ore pulp. The slime showed no change in dispersion and the pulp with a pH of 9.8+ was distinctly alkaline.

The results of this series of tests seem to indicate:

1. That lime is a dispersive agent. In these tests it not only affected the state of dispersion of the slime but also affected the adsorption of slime on the sulfide surfaces.

2. That zinc sulfate, potassium cyanide and copper sulfate are not dispersive agents. In these tests they did not affect the state of dispersion although used in amounts equal to those in practice. Further, at the magnifications used, they did not affect the slime coatings on the sulfides.

3. That the important factor in differential flotation is something other than control of slimes.

## Series II.—Bubble Tests on Slime-coated Particles

A full description of the bubble test and its use as a measure of the floatability of minerals can be found in the paper previously mentioned.[3]

Freshly broken particles of galena and sphalerite were tested in the bubble machine. The bubble showed the very slight adhesion and distortion common to slightly contaminated sulfide surfaces. These particles were then treated in the subaeration machine with −65-mesh Neihart ore in a 4 to 1 distilled-water pulp; no reagents were added. They were removed after 5 min. and washed in distilled water. Upon testing in the bubble machine, with a solution of 1 part in 40,000 potassium xanthate, there was no spreading of bubble on either particle. The collecting index in each case was zero. As will be seen later, a pure untreated piece of galena or sphalerite will give a collecting index of 30 or over in a potassium xanthate solution.

Particles of quartz and calcite tested in the bubble machine gave index numbers of zero with 1 part in 40,000 potassium xanthate solution. A set of bubble tests run with these two gangue minerals in solutions of

[3] A. F. Taggart, T. C. Taylor and C. R. Ince: *Op. cit.*

various collecting agents always gave the same result. Under no circumstances did the bubble machine indicate floatability.

Two more particles of galena and sphalerite were submitted to the bubble test in distilled water. They were then treated in a −65-mesh Neihart ore pulp with lime present in the proportion of 1.5 lb. per ton of solid. After removal they were washed in distilled water and tested in the bubble machine with 1 part in 40,000 potassium xanthate solution. No spreading resulted, the collecting indices therefore were zero.

It was shown in the tests in Series I that particles of lead and zinc sulfide when treated in a Neihart ore pulp became coated with a fairly heavy gangue-slime coating. Therefore it was not surprising that a

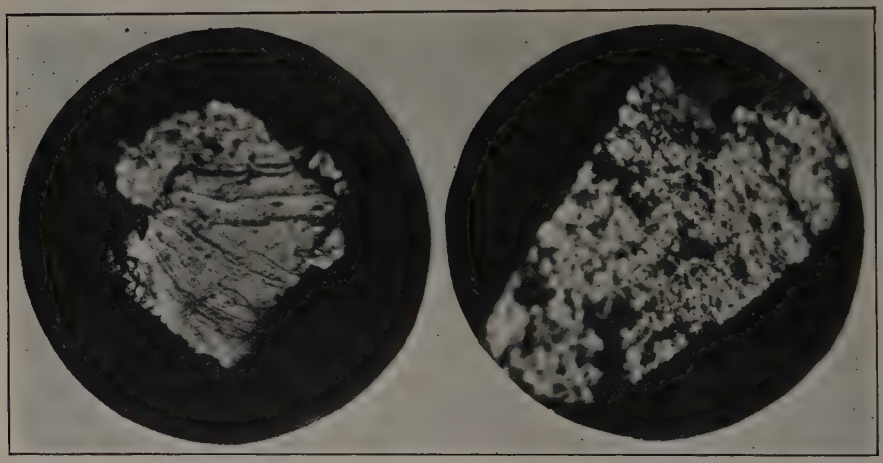

FIG. 7.—SPHALERITE PARTICLE IN CONCENTRATE OF FLOTATION TEST. × 240.

FIG. 8.—SPHALERITE PARTICLE IN TAILING OF FLOTATION TEST. × 240.

surface so altered should react to the bubble test as do gangue minerals such as quartz and calcite. However, the galena and sphalerite particles subjected to treatment in the Neihart ore pulp plus lime also showed no floatability by the bubble test, despite the fact that the results of the tests in Series I show the gangue-slime coating now to be much lighter than before. Here was a case where the bubble test was too sensitive a measure of floatability. Microscopic examination of flotation concentrate has shown that sulfide surfaces with slime coatings as slight as those of Figs. 5 and 6 will float with the usual amount of collecting and frothing agents. Fig. 7 is a photomicrograph of a sphalerite particle in a flotation concentrate. On the other hand, microscopic examination of sulfide surfaces in the tailings of a flotation test run with the usual amount of collecting and frothing agent showed that surfaces coated with slime to an extent comparable to the coatings obtained in Neihart ore pulp without lime would not float (see Fig. 2). Fig. 8 is a photomicrograph of a sphalerite particle in a flotation tailing.

## Series III.—Bubble Tests on Slime-free Particles

Bubble-machine tests were made on particles of galena and sphalerite. The relative collecting index of galena in a 1 part in 40,000 potassium xanthate solution was 100; that of sphalerite was 82. After agitation in a square glass-jar machine with solutions of 1 part in 16,000 of zinc sulfate and 1 part in 26,000 of potassium cyanide for 15 min., the particles were removed and again tested in the potassium xanthate solution. The relative collecting index of galena was 73 and that of sphalerite was 39.

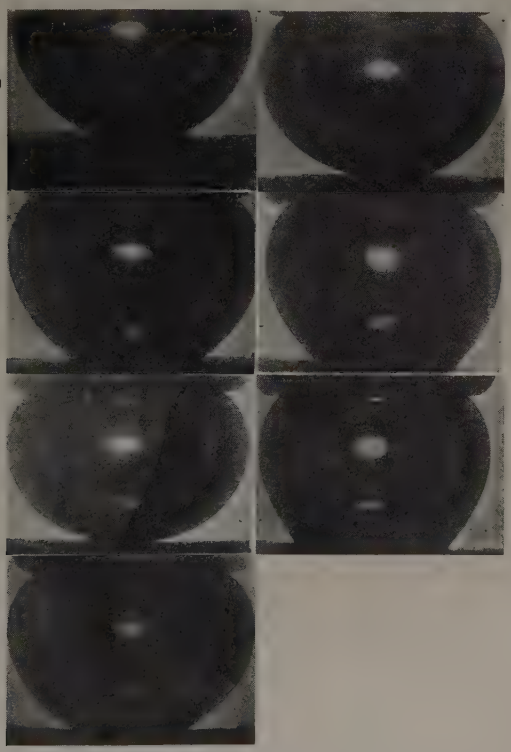


Fig. 9.—Sphalerite particle in distilled water.

Fig. 10.—Galena particle in distilled water.

Fig. 11.—Sphalerite particle in 1 part in 40,000 potassium xanthate solution. Relative collecting index, 59.

Fig. 12.—Galena particle in potassium xanthate solution. Relative collecting index, 100.

Fig. 13.—Sphalerite particle in potassium xanthate solution after treatment with potassium cyanide and zinc sulfate. Relative collecting index, 38. Depression of 164 per cent.

Fig. 14.—Galena particle in potassium xanthate solution after treatment with potassium cyanide and zinc sulfate. Relative collecting index, 100. No depression.

Fig. 15.—Sphalerite particle in potassium xanthate solution after treatment with copper sulfate. Relative collecting index, 45. Increase of 218 per cent.

This was a drop in floatability of 52 per cent. for sphalerite and of only 27 per cent. for galena. The two particles were then treated in the square

glass jar with a solution of 1 part in 2000 of copper sulfate for 5 min. Upon testing in the bubble machine with the potassium xanthate solution the collecting indices were 88 for galena and 57 for the sphalerite. This was an increase of 20 per cent. in the case of the galena and of 46 per cent. in the case of the sphalerite, showing that the sphalerite had been revived by the treatment with copper sulfate solution.

Further tests with sphalerite in the same manner showed these figures on the depression and revival of that sulfide to be conservative. In most cases the depression was between 100 and 150 per cent., whereas the increase in floatability after treatment with copper sulfate ran over 200 per cent.

A set of the preceding tests was run and the results were photographed (Figs. 9–15).

A similar set of tests was run with a sphalerite particle, using thiocresol as the collecting agent. The relative collecting index of sphalerite in a thiocresol solution (1 in 40,000) was 83. After the zinc sulfate and potassium cyanide treatment, the relative collecting index in the thiocresol was only 8.6. When treated in copper sulfate solution and tested in thiocresol, the relative collecting index was 86.

The results of this series of tests indicate that, without slime present, potassium cyanide and zinc sulfate in the amounts used in flotation depress sphalerite in the presence of galena while hardly, if at all, affecting the latter. The tests also indicate that copper sulfate may restore the floatability of sphalerite so depressed. The depressing effect observed in the tests may be obtained with potassium cyanide alone under proper conditions. In fact, field practice in certain localities is to use only cyanide as a depressant rather than the combination.

## Series IV.—Abstraction Tests

Abstraction of potassium cyanide by sulfides was first indicated by pH measurements. A 0.2 per cent. solution of potassium cyanide had a pH of 9.8+; *i. e.*, was strongly alkaline, due to hydrolytic dissociation of the KCN into KOH and HCN, a strong base and a weak acid. When the potassium cyanide was agitated by shaking in an Erlenmeyer flask with 15 g. of −65-mesh +200-mesh sphalerite and filtered, the filtrate had a pH of 7.0 or neutral, showing complete abstraction of potassium cyanide within the limits of accuracy of this method of measurement.

Further abstraction tests by galena and sphalerite in cyanide solutions were made by the silver nitrate method. With a 1 part in 10,000 potassium cyanide solution, 15 g. of −65-mesh +200-mesh sphalerite abstracted 90 per cent. With the same solution and similar conditions 27.5 g. of −65-mesh +200-mesh galena abstracted only 24.8 per cent. Sphalerite (15 g.) abstracted 17.5 per cent. of the cyanide from a 1 in 500 solution as against a 7.4 per cent. abstraction by galena (27.5 g.).

No quantitative measure was made of copper sulfate abstractions. The precipitate of copper xanthate produced by potassium xanthate in the presence of copper ion was used as an indicator. A definite amount of potassium xanthate solution when added to 100 c.c. of a 1 in 1000 copper sulfate solution gave a yellow precipitate. When the copper sulfate solution was agitated with 15 g. of −65 +200-mesh sphalerite and filtered, 100 c.c. of filtrate gave a yellow precipitate with the xanthate solution that was lighter than the previous one showing some abstraction of the $Cu^{++}$ ion. The copper sulfate solution was then agitated with −65 +200-mesh sphalerite which had previously been treated with a 1 in 10,000 potassium cyanide solution and filtered. Upon addition of a definite amount of the xanthate solution to 100 c.c. of the filtrate, a precipitate resulted which was distinctly lighter than either preceding one, showing that more of the $Cu^{++}$ ion had been abstracted on account of the presence of cyanide on the sphalerite surface.

Despite intensive microscopic study of the sulfide surfaces after treatment in solutions more concentrated than those used in the tests of potassium cyanide, zinc sulfate and copper sulfate, no surface alterations were visible at a magnification as high as 500.

### Series V.—Abstraction Tests with Collecting Agents

The most recent theory of collecting agents is that they concentrate at the sulfide-liquid interface with the molecule so oriented that the water-repelling groups which are common in all collecting agents are outward. Thus the particle now presents a surface that is water-repellent, rendering it easier of attachment by air bubbles and hence more floatable. The amount of this concentration is indicated by the abstraction of the collecting agent from solution.

The iodine-sodium thiosulfate method of analysis was used in the abstraction tests. After determining the iodine equivalent of the collecting agent present, 110 c.c. of the solution was agitated by shaking with the mineral for 5 min. in an Erlenmeyer flask. The contents of the flask were then filtered and a determination of the iodine equivalent of the collecting agent still remaining was made on 100 c.c. of the filtrate.

From a 1 in 35,000 thiocarbanilid solution, 27.5 g. of pure galena ground to −65 +200 mesh abstracted 23 per cent. of the collecting agent as compared to an abstraction of 18 per cent. by 15 g. of pure sphalerite ground to the same mesh. When the concentration of thiocarbanilid was increased to 1 in 20,000, galena abstracted 19 per cent. while sphalerite abstracted 12.8 per cent. Doubling the amount of galena increased the abstraction to 34.5 per cent.

From a 1 in 40,000 potassium xanthate solution 27.5 g. of −65 +200-mesh pure galena abstracted 76 per cent. and 15 g. of −65 +200-mesh pure sphalerite abstracted 21.5 per cent. and 24.0 per cent. Fifteen grams of sphalerite were treated at 140° F. with a potassium cyanide and

zinc sulfate solution of a strength equal to that found in flotation for 10 min. The sphalerite was then washed with distilled water twice and used for abstraction tests. From the 1 in 40,000 potassium xanthate solution the abstraction was only 5.8 per cent.

Abstraction tests by galena treated with Neihart ore pulp gave the following results. No lime was present, so presumably the slime coating was heavy. The method of treating these particles with slime was as follows: 27.5 g. of galena, sized between 65 and 200 mesh, was agitated with a 4 to 1 pulp of −200-mesh Neihart ore. The whole was then put on a 200-mesh screen and washed two or three times with distilled water. This left the slime-coated sulfide particles on the screen and washed through the free slimes. The galena was then used for the abstraction tests. From the 1 in 20,000 thiocarbanilid solution, 27.5 g. of slime-coated −65 +200-mesh galena abstracted 19.8 per cent.; 55 g. of slime-coated −65 +200-mesh galena abstracted 28.8 per cent.

Abstraction tests conducted with a gangue mineral indicated that there was only a slight tendency toward abstraction. Pure quartz, using 10 g. ground to −65 +200 mesh, abstracted 5.4 per cent. of the 1 in 20,000 thiocarbanilid solution; 20 g. of −65 +200-mesh quartz only increased the abstraction to 6.9 per cent.

The results of these abstraction tests are tabulated in Table 1. Despite the fact that, in order to approximate equal surface areas for abstraction comparisons, the material used was always sized between 65 and 200 mesh, and that allowance was made for the various specific gravities by using different weights of mineral, some difference in area

TABLE 1.—*Results of Abstraction Tests*

| Mineral | Amount Grams | Treatment of Mineral Previous to Abstraction Tests | Collecting-agent Solution | Per Cent. Abstracted |
|---|---|---|---|---|
| | | | Thiocarbanilid | |
| PbS..... | 27.5 | Ground to −65 +200 mesh | 1/35,000 | 23.0 |
| ZnS..... | 15 | Ground to −65 +200 mesh | 1/35,000 | 18.6 |
| ZnS..... | 15 | Ground to −65 +200 mesh | 1/20,000 | 12.8 |
| PbS..... | 27.5 | Ground to −65 +200 mesh | 1/20,000 | 19.0 |
| PbS..... | 55 | Ground to −65 +200 mesh | 1/20,000 | 34.5 |
| PbS..... | 27.5 | Exposed to Neihart ore pulp | 1/20,000 | 19.8 |
| PbS..... | 55 | Exposed to Neihart ore pulp | 1/20,000 | 28.8 |
| Quartz..... | 10 | Ground to −65 +200 mesh | 1/20,000 | 5.4 |
| Quartz..... | 20 | Ground to −65 +200 mesh | 1/20,000 | 6.9 |
| | | | Potassium xanthate | |
| PbS..... | 27.5 | Ground to −65 +200 mesh | 1/40,000 | 76.0 |
| ZnS..... | 15 | Ground to −65 +200 mesh | 1/40,000 | 21.5 |
| ZnS..... | 15 | Ground to −65 +200 mesh | 1/40,000 | 24.0 |
| ZnS..... | 15 | Conditioned in KCN and $ZnSO_4$ solution | 1/40,000 | 5.8 |

existed on account of dissimilarity in shapes of particles. That this difference in area could not account for differences in abstraction may be shown by consideration of the cyanide and xanthate abstractions by galena and sphalerite. In the cyanide abstraction tests 15 g. of the sized sphalerite abstracted four times as much as 27.5 g. of the sized galena, whereas in the xanthate abstraction 27.5 g. of galena abstracted 3.5 times as much as the 15 g. of sphalerite.

From Table 1 it can be seen that even the heaviest slime coating produced with Neihart ore did not affect the removal of the collecting agent despite the fact that gangue minerals abstract to a much less extent than sulfide. A possible explanation presents itself if one considers the relative sizes of slime particles and their distribution on the sulfide surface. Fig. 16 represents, on a large scale, a portion of a bubble and a sulfide surface with a Neihart-ore slime coating produced without lime present. It can be seen readily that although the slimes would

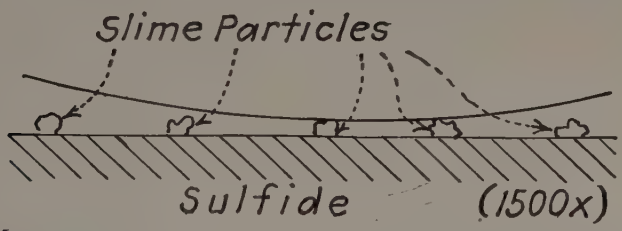


FIG. 16.—MAGNIFIED VIEW OF PORTION OF A BUBBLE AND A SULFIDE SURFACE WITH A NEIHART-ORE SLIME COATING PRODUCED WITHOUT LIME.

not interfere much with the abstraction of the collecting agent (the little dots on the surface represent collecting-agent molecules—really about 100 times too big) all or part of the slime would have to be removed to allow the bubble to come in contact with the water-repellent groups of the molecules of the collecting agent.

Up to this point the investigation dealt entirely with the effects of the various reagents on the constituents of a flotation pulp. The next step was to investigate the reasons for the effects produced.

In the paper previously mentioned,[4] the hypothesis is advanced that partial oxidation must take place at the sulfide surface before collecting agents can act thereon and that the collecting agent reacts with the more soluble oxidized salt of the metal to form an insoluble compound. Hydrolysis or oxidation is indicated when lead or zinc sulfide is ground in water in the presence of air, as was shown by the following experiment: 100 g. of −65 +200-mesh galena was ground with 70 c.c. of distilled water in a porcelain mill with porcelain balls. The mill was stopped at regular intervals and a sample of water was taken for pH measurement:

[4] A. F. Taggart, T. C. Taylor and C. R. Ince: *Op. cit.*

| Time, Minutes | pH |
|---|---|
| At start | 7.0 |
| 10 | 6.8 |
| 30 | 6.6 |
| 50 | 6.4 |
| 110 | 5.8 |

The same test was repeated with sphalerite:

| | |
|---|---|
| At start | 7.0 |
| 30 | 9.8+ |

That galena abstracted more of the collecting agent might be accounted for in that its surface alteration produced by the chemical action of air and water may be more soluble than that of the sphalerite and that the lead compounds resulting from the reaction of the collecting agent with the soluble altered galena surface have a lower solubility product and therefore tend to form more readily than the zinc compounds.

Table 1 shows that treatment by cyanide of a sulfide decreases the abstraction of the collecting agent and consequently the floatability of that sulfide surface. It has also been shown that sphalerite abstracts potassium cyanide from solution much more readily than does galena. Mellor[5] says that sphalerite oxidizes faster than galena and slower than iron pyrite. This becomes significant when it is noticed that the order of depressability by potassium cyanide is in the reverse ratio; that is, iron pyrite is depressed more easily than sphalerite and sphalerite more easily than galena. Galena practically is not depressed at all by potassium cyanide. Clennell[6] says that no simple cyanide of lead is known. On the other hand, alkali cyanides react readily with the metals and salts of zinc and iron. The action of potassium cyanide with a zinc salt results in the simple cyanide of zinc, which is insoluble.

$$2KCN + Zn^{++} \rightarrow 2K^{+} + ZnCN_2$$

It is quite possible that if such a compound forms at the sphalerite surface, despite the fact that microscopic examination has shown that it is not visible, it may prevent the reaction with the collecting agent. Since the zinc would be anchored in the lattice of the sphalerite crystal the CN end of the molecule is presented to the solution. CN being a strong water-avid group, this probably accounts for the difficult floatability of the particle.

Upon the addition of copper sulfate to a solution containing sulfide surfaces thus altered, copper ion is removed, as shown by the abstraction tests in Series IV. A possible explanation of this is that there is present to some extent at the solid-liquid interface the ions $Cu^{++}$, $CN^{-}$ and $SO_4^{++}$. The zinc, held in the structure of the solid particle, is not mobile. The

[5] J. W. Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry. London and New York, 1922–28. Longmans, Green & Co.

[6] J. E. Clennell: The Cyanide Handbook. New York, 1915. McGraw-Hill Book Co.

$Cu^{++}$ ion unites with $CN^-$ to form the insoluble $CuCN_2$ and precipitates as such. The reaction carried to completion removes the CN from the particle surface, leaving the unsatisfied zinc free to unite with the sulfate ions present to form a zinc sulfate surface, which now can react with the collecting agent.

## Series VI.—Migration of Slime Particles

Tests in Series I show that Neihart ore pulp will coat sulfide particles with a slime coating of a certain density. The presence of lime in the pulp decreases the density of this coating at least one-half and renders the sulfide surface floatable where previously it was not floatable. The reason for this slime adsorption and the effect of lime upon it is of paramount importance.

Solid-solid adsorption is thought to be an electrical phenomenon dependent entirely on the charge existing in the adsorbing surface and the absorbed solid. Flocculation is a form of solid-solid adsorption in which particles in suspension coagulate to form larger masses of the particles. Dispersion, the opposite of flocculation, is therefore also dependent on the electrical charges existing on the suspended solids. Any reagent that affects the degree of dispersion of the slime particles may therefore be expected to affect the adsorption of the gangue on the sulfide surfaces. This fact has been noted in the experimental work performed.

To determine the electrical charges on solid particles, the Burton tube was used. Two other methods had been attempted and failed. The first was the glass cell used by Beans and Eastlack[7] in their work with colloidal gold. This was used with a microscope. This method was discarded because of the enormous errors introduced by endosmose and the apparent inconsistencies resulting therefrom. The other method was the observance with a photomicrographic apparatus of a stream of slime particles settling under gravity between two platinum-strip electrodes. It was thought that the particles would swerve from the perpendicular fall when a potential difference existed between the electrodes. The direction of swerve would indicate the charge. The difficulty in this case was that, despite protection of the bulk of the liquid from chemical action at the electrodes, the generation of gases was enough to set up currents which caused the particles to move erratically in any direction. Some indication of charge was given by an initial jump of the particles when the voltage was thrown on but, since the gaseous disturbances started almost immediately, the evidence was not conclusive enough and was discarded when the Burton tube method proved successful. A sketch of the Burton-tube apparatus is shown in Fig. 17.

[7] H. T. Beans and H. E. Eastlack: The Electrical Synthesis of Colloids. *Jnl.* Amer. Chem. Soc. (1915) **37**, 2667.

The procedure in each case was as follows: The stopcock *B* was closed and the Burton tube *C* filled with distilled water to the depth of about 3 cm. in each arm of the tube. The thistle tube *A* contained the slime suspension. Stopcock *B* was slowly opened and the slime suspension allowed to rise in the Burton tube. If this was done carefully and without jarring there was a distinct boundary between the gray cloud of the suspension and the distilled water. The stopcock was closed as soon as the rising slime suspension had caused the platinum electrodes to become immersed in the distilled water. Due to gravity, the slime suspension in

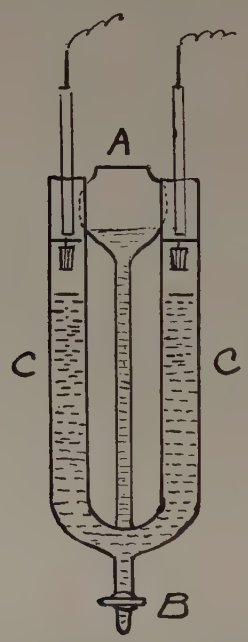


Fig. 17.—Burton-tube apparatus.

both sides of the tube would settle at the same rate. If, however, a voltage difference existed between the electrodes and the particles in the suspension had a definite electrical charge, there would be a difference in settling rate in the two arms. In one arm of the tube the tendency to migrate toward the electrode, due to charge, would assist the natural fall of gravity. In the other arm it would retard the fall of gravity. Consequently, one arm would settle fast and the other arm slowly, if at all. Knowing which arm was the cathode and which the anode, the charge of the particle would be indicated by this differential settling.

In preparing a slime suspension 10 to 20 g. of +65-mesh solid was ground in a porcelain mortar with a porcelain pestle, having present 40 to 80 c.c. of the liquid to be used for the suspending medium. After 2 min.

settling in a 100 c.c. beaker the material still in suspension was used for the test.

A series of slime-migration experiments is given under tests 1 to 15 and the results are tabulated in Table 2.

The graduations on the arms of the Burton tube read from top to bottom. The numbers given in tests 1 to 15 under anode arm and cathode arm represent readings of the slime-suspension boundary at the time indicated on the left. The difference between any two succeeding readings gives the rate of settling for that interval. Where the slime boundary moved upward this difference would naturally be negative. Looking at test 1, it is seen that the differences in the anode arm are negative, *i. e.*, the slime boundary was rising in that arm; while in the cathode arm the differences are positive, showing a distinct settling of the slime. Obviously the slime was moving toward the anode and is therefore negatively charged.

TEST 1

NEIHART SLIME IN DISTILLED WATER

119 Volts

| Time of Reading | Anode Arm | | Cathode Arm | |
|---|---|---|---|---|
| 10:35 | 4.2 | | 3.0 | |
| | | +0.4 diff. | | +0.4 diff. |
| 10:40 | 4.6 | | 3.4 | |
| | | −0.2 diff. | | +1.6 diff. |
| 10:45 | 4.4 | | 5.0 | |
| | | −0.2 diff. | | +1.2 diff. |
| 10:50 | 4.2 | | 6.2 | |

Voltage Reversed after 10:50 Reading

| | Cathode Arm | | Anode Arm | |
|---|---|---|---|---|
| | | | Settled out | |
| | | | Boundary indistinct | |
| 10:55 | 4.2 | | | |
| | | +0.4 diff. | | −0.6 diff. |
| 11:00 | 4.6 | | | |
| | | +0.2 diff. | | |
| 11:05 | 4.8 | | | |
| 11:10 | 5.0 | +0.2 diff. | 5.6 | |
| 11:15 | 5.2 | | 5.5 | |
| | | +0.2 diff. | | −0.1 diff. |

Migration was anionic, indicating a negative slime.

TEST 2

NEIHART SLIME IN DISTILLED WATER

243 Volts, 0.001 Ampere

| Time of Reading | Anode Arm | | Cathode Arm | |
|---|---|---|---|---|
| 10:47 | 4.0 | | 4.6 | |
| | | +0.8 | | +1.8 |
| 10:52 | 4.8 | | 6.4 | |

Reversed Voltage, 244 Volts, 0.001 Ampere

| | Cathode Arm | | Anode Arm | |
|---|---|---|---|---|
| 10:57 | 5.2 | | 6.4 | |
| | | +0.6 | | 0.0 |
| 11:02 | 5.8 | | 6.4 | |

The boundaries became so indistinct as to make further readings unreliable. Migration was anionic, showing the slime was negative. The conductivity increased as the experiment progressed in the case of slime suspensions made of oxidized material. Those of freshly ground material had a much lower specific conductivity.

### Test 3

### Anaconda Slime in Distilled Water

237 Volts, 0.0045 Ampere

| Time of Reading | Anode Arm | | Cathode Arm | |
|---|---|---|---|---|
| 3:35 | 4.6 | | 5.8 | |
| | | −0.1 | | +0.2 |
| 3:40 | 4.5 | | 6.0 | |
| | | −0.1 | | +0.4 |
| 3:45 | 4.4 | | 6.4 | |
| | | 0.0 | | +0.2 |
| 3:46 | 4.4 | | 6.6 | |
| | | −0.2 | | +0.2 |
| 3:49 | 4.2 | | 6.8 | |

Reversed Voltage, 239 Volts, 0.003 Ampere

| | Cathode Arm | | Anode Arm | |
|---|---|---|---|---|
| 3:51 | 4.2 | | 7.0 | |
| | | +0.4 | | 0.0 |
| 3:53 | 4.6 | | 7.0 | |
| | | +0.8 | | −0.2 |
| 3:58 | 5.4 | | 6.8 | |
| | | +1.4 | | 0.0 |
| 4:03 | 6.8 | | 6.8 | |

Migration was anionic, indicating a negative slime.

### Test 4

### Anaconda Slime in Distilled Water + Lime (1/2000 on Solid)

234 Volts

| Time of Reading | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 4:20 | 4.4 | | 0.008 | 5.6 | |
| | | +0.6 | | | +0.2 |
| 4:23 | 5.0 | | 0.007 | 5.8 | |
| | | −0.2 | | | 0 |
| 4:26 | 4.8 | | 0.010 | 5.8 | |
| | | +0.2 | | | −0.2 |
| 4:29 | 5.0 | | 0.014 | 5.6 | |
| | | 0.0 | | | +0.2 |
| 4:32 | 5.0 | | 0.016 | 5.8 | |
| | | 0.0 | | | +0.6 |
| 4:35 | 5.0 | | 0.018 | 6.4 | |

Reversed Voltage, 240 Volts

| | Anode Arm | Amperes | Cathode Arm | |
|---|---|---|---|---|
| 4:36 | Flocculent | 0.016 | 6.4 | |
| | | | | −0.6 |
| 4:39 | Masses | 0.014 | 5.8 | |
| | | | | 0 |
| 4:42 | | 0.012 | 5.8 | |

The migration in this case appeared to be cationic, but was obscured by flocculation The slime was therefore positive.

### Test 5

### Quartz in Distilled Water

234 Volts

| Time of Reading | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 1:44 | 5.0 | | 0.001 | 5.0 | |
| | | +1.2 | | | +0.1 |
| 1:47 | 6.2 | | 0.0015 | 5.1 | |
| | | +1.6 | | | 0 |
| 1:50 | 7.8 | | 0.002 | 5.0 | |

Reversed Voltage, 236 Volts

| | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 1:53 | 6.2 | | 0.0015 | 5.0 | |
| | | −0.2 | | | +0.4 |
| 1:56 | 6.0 | | 0.0015 | 5.4 | |
| | | 0 | | | +0.6 |
| 2:01 | 6.0 | | 0.002 | 6.0 | |
| | | 0 | | | +1.3 |
| 2:04 | 6.0 | | 0.0025 | 7.3 | |
| 2:07 | | | | | |

Reversed Voltage, 238 Volts

| | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 2:10 | 6.2 | | 0.0015 | 7.4 | |
| 2:13 | * | +0.6 | * | * | −0.9 |
| 2:16 | 6.8 | | 0.0015 | 6.5 | |

Migration was anionic, showing quartz slime-suspension was negative.

* No Observation Made—Detached Wire.

### Test 6
### Quartz in Distilled Water + Lime (1/2000 on Solid)

239 Volts

| Time of Reading | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 2:52 | 6.0 | | 0.001 | 5.4 | |
| | | +0.4 | | | +0.4 |
| 2:55 | 6.4 | | 0.0015 | 5.8 | |
| | | +0.2 | | | 0.0 |
| 2:58 | 6.6 | | 0.003 | 5.8 | |
| | | +0.2 | | | −0.2 |
| 3:01 | 6.8 | | 0.004 | 5.6 | |
| | | +0.2 | | | 0 |
| 3:04 | 7.0 | | 0.004 | 5.6 | |
| | | +0.2 | | | −0.2 |
| 3:07 | 7.2 | | 0.004 | 5.4 | |

Reversed Voltage, 247 Volts

| | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 3:10 | 7.2 | | 0.0025 | 5.8 | |
| | | +0.2 | | | +0.4 |
| 3:13 | 7.4 | | 0.0025 | 6.2 | |
| | | +0.1 | | | +0.2 |
| 3:16 | 7.5 | | 0.003 | 6.4 | |
| | | −0.1 | | | +0.2 |
| 3:19 | 7.4 | | 0.0025 | 6.6 | |

Migration was cationic, showing that quartz slime in the presence of lime was positive.

A galena experiment failed. A heavy suspension settled out too quickly. A light suspension was indistinguishable at the boundary line.

### Test 7
### Sphalerite in Distilled Water

234 Volts

| Time of Reading | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 5:30 | 7.2 | | 0.0005 | 6.0 | |
| | | −0.2 | | | +0.3 |
| 5:33 | 7.0 | | 0.0005 | 6.3 | |
| | | −0.1 | | | +0.2 |
| 5:36 | 6.9 | | 0.0005 | 6.5 | |
| | | −0.1 | | | +0.1 |
| 5:39 | 6.8 | | 0.0008 | 6.6 | |
| | | −0.1 | | | 0 |
| 5:42 | 6.7 | | | 6.6 | |

Reversed Voltage—234 Volts

| | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 5:45 | 6.8 | | 0.0005 | 6.6 | |
| | | +0.4 | | | −0.1 |
| 5:48 | 7.2 | | 0.0005 | 6.5 | |
| | | +0.2 | | | −0.1 |
| 5:51 | 7.4 | | 0.0005 | 6.4 | |
| | | +0.1 | | | 0 |
| 5:53 | 7.5 | | 0.0005 | 6.4 | |
| | | +0.1 | | | +0.1 |
| 5:56 | 7.6 | | | 6.5 | |

Migration was anionic, indicating that sphalerite in distilled water was negative.

Voltage was kept on for ½ hr. after conclusion of readings. The cathode tube settled out and amperage went to 0.0015.

### Test 8
### Sphalerite in Distilled Water + Lime (1/2000 on Solid)

230 Volts

| Time of Reading | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 6:49 | 6.4 | | 0.0005 | 6.1 | |
| | | +0.5 | | | +0.3 |
| 6:51 | 6.9 | | 0.0005 | 6.4 | |
| | | +0.3 | | | 0 |
| 6:54 | 7.2 | | 0.0005 | 6.4 | |
| | | +0.2 | | | 0 |
| 6:57 | 7.4 | | 0.0005 | 6.4 | |

Reversed Voltage, 236 Volts

| | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 7:00 | 7.2 | | 0.0005 | 6.2 | |
| | | 0 | | | +0.2 |
| 7:03 | 7.2 | | 0.0005 | 6.4 | |
| | | 0 | | | +0.1 |
| 7:06 | 7.2 | | 0.0005 | 6.5 | |
| | | 0 | | | 0 |
| 7:09 | 7.2 | | 0.0008 | 6.5 | |

Migration was anionic, showing that sphalerite in the presence of lime was negative.

### Test 9

### Neihart Slime in Distilled Water

234 Volt pH = 6.8

| Time of Reading Minutes | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 0 | 7.2 | | 0.001 | 6.2 | |
| | | −0.2 | | | +0.6 |
| 3 | 7.0 | | 0.001 | 6.8 | |
| | | 0 | | | +0.2 |
| 6 | 7.0 | | 0.0013 | 7.0 | |
| | | 0 | | | +0.4 |
| 9 | 7.0 | | 0.0018 | 7.4 | |
| | | 0 | | | +0.2 |
| 12 | 7.0 | | 0.0025 | 7.6 | |

Reversed Voltage, 232 Volts, 0.0023 Ampere

| | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 15 | 7.2 | | 0.0015 | 7.4 | |
| | | +0.2 | | | −0.2 |
| 18 | 7.4 | | 0.0015 | 7.2 | |
| | | +0.2 | | | 0 |
| 21 | 7.6 | | 0.0018 | 7.2 | |

Migration was anionic. Neihart slime in distilled water was therefore negative.

This test confirmed the earlier one on the same material at 119 volts. In another test both arms were filled to electrode with the suspension and the voltage thrown on. After 20 min., in which there was a gradual flocculation, the cathode arm settled out.

### Test 10

### Neihart Ore in Distilled Water + Lime (1.5/2000 on Solid)

240 Volts

| Time of Reading, Minutes | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 0 | 4.4 | | 0.0015 | 5.0 | |
| | | +0.6 | | | +0.4 |
| 1.5 | 5.0 | | 0.0020 | 5.4 | |
| | | +0.2 | | | +0.2 |
| 3 | 5.2 | | 0.0023 | 5.6 | |
| | | −0.2 | | | +0.4 |
| 6 | 5.0 | | 0.0035 | 6.0 | |
| | | 0 | | | +0.3 |
| 9 | 5.0 | | 0.0045 | 6.3 | |

Migration was anionic and slime was negative.

### Repeat on Neihart Ore

### Neihart Ore in Distilled Water + Lime (1.5/2000 on Solid) + Calcium Chloride (1/2000 on Solid)

230 Volts

| Time of Reading, Minutes | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 0 | 5.7 | | 0.003 | 5.8 | |
| | | +0.7 | | | +0.6 |
| 3 | 6.4 | | 0.0045 | 6.4 | |
| | | +0.5 | | | −0.4 |
| 6 | 6.9 | | 0.0075 | 6.0 | |
| | | +0.5 | | | −0.6 |
| 9 | 7.4 | | 0.012 | 5.4 | |

Reversed Voltage, 230 Volts

| | Anode Arm | | Amperes | Cathode Arm |
|---|---|---|---|---|
| 12 | 7.2 | | 0.0095 | 5.4 |
| | | +0.4 | | |
| 15 | 7.6 | | * electrode exposed | |

Migration was anionic, slime was negative.

### Repeat on Neihart Ore

In distilled water with calcium chloride and lime present in amounts shown in preceding test.

236 Volts

| Time of Reading, Minutes | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 0 | 4.6 | | 0.002 | 4.2 | |
| | | +0.8 | | | +0.2 |
| 1.5 | 5.4 | | 0.002 | 4.4 | |

Reversed Voltage

| Time of Reading, Minutes | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 3 | 5.4 | | 0.002 | 4.8 | |
| | | +0.2 | | | +0.6 |
| 6 | 5.6 | | 0.004 | 5.4 | |
| | | +0.2 | | | +0.6 |
| 9 | 5.8 | | 0.0045 | 6.0 | |
| | | +0 | | | +0.2 |
| 12 | 5.8 | | 0.0045 | 6.2 | |
| | | +0.1 | | | +0.4 |
| 15 | 5.9 | | 0.0055 | 6.6 | |

Migration was anionic, therefore slime was negative.

### Test 11

An attempt was made to determine the charge on galena (−65 mesh freshly ground) suspended in distilled water. The suspension was allowed to flow into both arms of the tube until the electrodes were submerged. The voltage was thrown on and the relative speed of settling of the arms observed:

1st observation, cathode cleared first.
2nd observation, cathode cleared first.
3rd observation, cathode cleared first.
Galena in distilled water was negative.

The presence of lime in the distilled water gave the same result. The cathode cleared first, indicating that the galena was negative in alkaline distilled water.

The preceding tests were repeated, using Neihart slime water instead of distilled water as the suspension medium.

1st observation, anode settled first.
2nd observation, anode settled first.
Galena in Neihart slime water was positive.

### Test 12

Sphalerite in Neihart Slime Water

240 Volts

| Time, Minutes | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 0 | 3.2 | | 0.004 | 3.6 | 0 |
| | | +0.8 | | | |
| 3 | 4.0 | | 0.0045 | 3.6 | |
| | | +1.6 | | | −0.6 |
| 6 | 5.6 | | 0.0050 | 3.0 | |

Reversed Voltage

| | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 9 | 7.0 | | 0.005 | 3.0 | |
| | | −2.0 | | | +3.2 |
| 12 | 5.0 | | | 6.2 | |

Migration was distinctly cationic and very rapid. Sphalerite suspended in Neihart slime water was positive.

### Test 13

Neihart slime water was prepared by grinding 60 g. −65-mesh Neihart ore in 240 c.c. of distilled water with lime (0.045 g.) and calcium chloride (0.03 g.). Sphalerite suspended in filtrate for migration test.

240 Volts pH 9.8+

| Time, Minutes | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 0 | 3.8 | | 0.0095 | 4.8 | |
| | | 4.0 | | | +0.2 |
| 3 | 7.8 | | 0.0105 | 5.0 | |

Migration very distinct

Voltage reversed with boundaries at

| Time, Minutes | Anode Arm | Amperes | Cathode Arm | |
|---|---|---|---|---|
| | 10.0 | 0.011 | 5.0 | |
| | | | | +2.4 |
| 6 | Suspension started to rise but the whole arm became cloudy as boundary line faded | | 7.4 | |

Migration was anionic, showing that sphalerite in alkaline Neihart slime water was negative.

### Test 14

Neihart Ore Suspended in Neihart Slime Water + Lime (1.5/2000 on Solid) and Calcium Chloride (1/2000 on Solid)

240 Volts

| Time, Minutes | Anode Arm | | Amperes | Cathode Arm | |
|---|---|---|---|---|---|
| 0 | 3.4 | | 0.008 | 4.6 | |
| | | +0.6 | | | +0.9 |
| 1 | 4.0 | | 0.009 | 5.5 | |
| | | +0.5 | | | +0.5 |
| 2 | 4.5 | | 0.009 | 6.0 | |
| | | +0.5 | | | +0.4 |
| 3 | 5.0 | | 0.0095 | 6.4 | |
| | | +0.6 | | | +0.8 |
| 4 | 5.6 | | 0.0095 | 7.2 | |
| | | +0.9 | | | +1.2 |
| 5 | 6.5 | | 0.0095 | 8.4 | |
| | | +0.7 | | | +1.1 |
| 6 | 7.2 | | 0.0095 | 9.5 | |

Reversed Voltage

| | Cathode Arm | | | Anode Arm | |
|---|---|---|---|---|---|
| 7 | 8.0 | | | 10.0 | |
| | | +0.2 | | | −2.0 |
| 8 | 8.2 | | | 8.0 | |

Migration was anionic, indicating that Neihart slime particles with lime and calcium chloride present were negative.

### Test 15

Galena in Neihart Slime Water with Lime and Calcium Chloride in Usual Amounts

240 Volts

| Time, Minutes | Cathode Arm | | Amperes | Anode Arm | |
|---|---|---|---|---|---|
| 0 | 6.0 | | 0.01 | 4.4 | |
| | | +0.5 | | | +0.2 |
| 1 | 6.5 | | 0.01 | 4.6 | |
| | | +0.5 | | | +0.2 |
| 2 | 7.0 | | 0.01 | 4.8 | |

Reversed at

| | | | | | |
|---|---|---|---|---|---|
| 3 | 7.5 | | | 5.3 | |
| | Anode Arm | | Amperes | Cathode Arm | |
| 4 | 8.0 | | | 6.5 | |
| | | −0.5 | | | +1.7 |
| 5 | 7.5 | | | 8.2 | |
| | | | | | +2.1 |
| 6 | Indistinct Boundary | | 0.011 | 10.3 | |

Migration was anionic, showing that galena in alkaline Neihart slime water was negative.

The Neihart slime water used in these tests probably differs from the mill water used in the flotation circuit at Timber Butte mill. The presence of soluble salts makes the latter much more acid than that indicated by the pH of 6.8 for the former. For that reason the amount of lime used in these tests was more than necessary. The same amount of lime used at Timber Butte mill only brought their alkalinity to a pH of 8.2–8.4 whereas the slime water used here became greater than 9.8.

TABLE 2.—*Results of Slime-migration Experiments*

| Test Number | Material | Medium of Suspension | Charge | pH |
|---|---|---|---|---|
| 3 | Anaconda ore | Distilled water | − | 7.0 |
| 4 | Anaconda ore | Distilled water + CaO[a] | + | 9.8+ |
| 5 | Quartz | Distilled water | − | 7.0 |
| 6 | Quartz | Distilled water + CaO[a] | + | 9.8+ |
| 7 | Sphalerite | Distilled water | − | 7.0 |
| 8 | Sphalerite | Distilled water + CaO[a] | − | 9.8+ |
| 11 | Galena | Distilled water | − | 7.0 |
| 11 | Galena | Distilled water + CaO[a] | − | 9.8+ |
| 11 | Galena | Neihart slime water | + | 6.8 |
| 15 | Galena | Neihart slime water + CaO, $CaCl_2$[b] | − | 9.8+ |
| 12 | Sphalerite | Neihart slime water | + | 6.8 |
| 13 | Sphalerite | Neihart slime water + CaO, $CaCl_2$[b] | − | 9.8+ |
| 1, 2, 9 | Neihart ore | Distilled water, Neihart slime water | − | 6.8 |
| 10, 14 | Neihart ore | Distilled water, Neihart slime water, + CaO, $CaCl_2$[b] | − | 9.8+ |

[a] 1.0 to 1.5 lb. per ton of solid.
[b] 1 lb. per ton of solid.

Slime adsorption tests similar to those found in Series I were run using quartz slime instead of the Neihart ore slime. Figs. 18 to 21 show the slime coatings obtained. These results combined with those of Series I and VI are tabulated in Table 3.

TABLE 3.—*Results of Slime-adsorption Tests*

| Adsorbed Material | Charge | Adsorbing Material | Charge | Suspension Medium | Relative Slime Coating | Photo-micro-graph |
|---|---|---|---|---|---|---|
| Quartz | − | Galena | − | Distilled water | Light | Fig. 18 |
| Quartz | − | Sphalerite | − | Distilled water | Light | Fig. 19 |
| Quartz | + | Galena | − | Distilled water +CaO | Heavy | Fig. 20 |
| Quartz | + | Sphalerite | − | Distilled water +CaO | Heavy | Fig. 21 |
| Neihart ore | − | Galena | + | Neihart slime water | Heavy | Fig. 1 |
| Neihart ore | − | Sphalerite | + | Neihart slime water | Heavy | Fig. 2 |
| Neihart ore | − | Galena | − | Neihart slime water +CaO, $CaCl_2$ | Light | Fig. 5 |
| Neihart ore | − | Sphalerite | − | Neihart slime water +CaO, $CaCl_2$ | Light | Fig. 6 |

## SUMMARY

1. Slimes do or do not coat sulfide particles according to the electrical charges existing on the surfaces of the two types of particles.

2. The nature and magnitude of the electrical charge may be altered by dispersion agents.

3. The amount of slime coating can be controlled by means of dispersion agents.

4. A slime-coated sulfide does not float as readily as one that is slime-free.

5. The floatability of a particle depends in part on the presence of collecting agent at its surface.

6. Cyanide and zinc sulfate do not affect slime coatings.

FIG. 18.—QUARTZ SLIME COATING, GALENA SURFACE.
FIG. 19.—QUARTZ SLIME COATING, SPHALERITE SURFACE.
FIG. 20.—QUARTZ SLIME PLUS LIME ($\frac{1}{2000}$ ON SOLID), GALENA SURFACE.
FIG. 21.—QUARTZ SLIME PLUS LIME ($\frac{1}{2000}$ ON SOLID), SPHALERITE SURFACE.

7. Cyanide and zinc sulfate decrease the concentration of collecting agent at the surface of certain sulfides, thereby rendering them less floatable.

8. Copper sulfate is capable of restoring the floatability by permitting the concentration of collecting agent at the sulfide surface.

## DISCUSSION

A. M. GAUDIN, Salt Lake City, Utah (written discussion).—Mr. Ince presents some valuable observations: *i.e.*, the records of slime-migration tests given under

headings 1 to 15 inclusive, as well as his correlations of the slime migration tests with the pH of the pulp and with the relative slime coating on galena and on sphalerite (Tables 2 and 3).

The correlation of slime coatings on comparatively coarse solids with the sign of the charge on the coated solid and that on the slime is a valuable contribution for which the author deserves credit. As one might expect, his results indicate that a positively charged sulfide attracts a negatively charged slime, and vice versa. It is interesting to note that all the minerals tested by Mr. Ince were negatively charged in distilled water. This suggests that one certain ion, no doubt the hydroxyl ion, is responsible for the charge. The change in the pH of pulps by clean, unoxidized sulfides has been found[8] to be in the direction of lesser pH, as would be expected if hydroxyl ions were removed from solution by the minerals.

It is to be regretted that no chemical or mineralogical analysis of the Neihart ore is given. It is also to be regretted that no analysis of the Neihart slime water is given and that apparently no attempt has been made to size the slime by elutriation or under the microscope. Analytical data of that nature might go a long way toward explaining the phenomena discussed by Mr. Ince.

The author's second conclusion, that "the nature and magnitude of the electrical charge may be altered by dispersion agents," is too sweeping in view of his evidence, which is limited to lime and to lime in the presence of calcium chloride, although it may well be justified. Similarly his third conclusion, "The amount of slime coating can be controlled by means of dispersion agents," is barely justified, as can be seen by referring in detail to the text under Series I, where the author shows no change in slime coating due to the subsequent addition of lime to the ore pulp, and but slight change due to previous addition of lime. This is all the evidence recorded to justify the above quoted conclusion, which is in implied contradiction with the author's summary of the results of his slime-coating investigation, that "the important factor in differential flotation is something other than control of slimes."

The author's determinations of the floatability of galena and sphalerite particles by means of the "bubble machine" are unconvincing. They are, also, in apparent disagreement with the tentative conclusions obtained with the slime-coating experiments. Mr. Ince feels that this is due to the fact that the "bubble test was too sensitive a measure of floatability." To one not versed in the details of the manipulation of the bubble machine it would appear that the opposite might be equally true.

Concerning the chemical aspects of the author's study, it is necessary to take exception to a number of statements: For instance, copper forms a cuprous cyanide rather than a cupric cyanide. Cuprous cyanide is comparatively insoluble in water, but is soluble in excess cyanide, forming a complex salt involving the cuprocyanide ion[9] $Cu(CN)^{--}_3$. The same is true of zinc cyanide, which forms complex zinc-cyanide ions in the presence of excess cyanide.

Mr. Ince states that copper sulfate is a depressing agent. Our experience has consistently indicated the converse to be true, except, perhaps, in what concerns the flotation of pyrite. An investigation of the flotation of sphalerite has been under way at the University of Utah for the past year and a half, and a manuscript covering this work is being prepared.[10] In some respects, as for instance in what concerns the

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[8] A. M. Gaudin: The Influence of Hydrogen-ion Concentration on Recovery in Simple Flotation Systems. *Min. & Met.* (1929) 10, 19.

[9] W. D. Bonner and S. Ravitz. *Jnl.* Amer. Chem. Soc.

[10] A. M. Gaudin, E. C. Haas and C. B. Haynes: Flotation Fundamentals, IV. Utah Eng. Expt. Sta. *Tech. Pub.* 8.

A. M. Gaudin: Effect of Xanthates, Copper Sulfate and Cyanide on Flotation of Sphalerite. See page 417, this volume.

abstraction of copper sulfate from solution by sphalerite, we have obtained extremely interesting data. In this connection it might be noted that sphalerite is discolored by treatment with copper sulfate, assuming a covellite color after a few hours treatment in hot normal copper sulfate solution about 150°C. This is in disagreement with Mr. Ince's statement that no surface alterations, due to copper sulfate treatment, were visible on sphalerite at a magnification as high as 500.

# Experiments with Flotation Reagents

By Arthur F. Taggart,* T. C. Taylor† and C. R. Ince,‡ New York, N. Y.

(New York Meeting, February, 1929)

The following notes represent significant excerpts from a mass of records of experimental work done in the ore-dressing laboratory at the Columbia School of Mines during the years 1926 to 1928 inclusive.

## Classification of Experimental Work

The experiments performed may be grouped for purposes of description under the following general headings:

I. Collecting agents.
   a. A method for quantifying collecting effect.
   b. Coating with undissolved collecting agents (oils).
   c. Action of dissolved collecting agents.

II. Frothing agents.
   a. A method for quantifying frothing effect.
   b. Relation between frothing effect and chemical composition.

III. Inorganic reagents.
   a. Methods of studying the effects of these reagents.
   b. Effect on slime dispersion.
   c. Effect on sulfides.

## Summary of the Origins of Present-day Flotation Practice

The first practicable, foolproof method of froth flotation was described in U. S. Patent 835120, issued in 1906 to Sulman, Picard and Ballot, and in the equivalent patents in other countries. A number of less simple methods of producing the same result had been described previously in patent publications and otherwise.[1] The reagents specified in all of these early patents were "oils" and, in addition, some inorganic substance, usually an acid. The quantities of reagents recommended and added were enormous when compared with those used today.

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[1] A. F. Taggart: Handbook of Ore Dressing, 790. New York and London, 1927, John Wiley & Sons, Inc.; Chapman & Hall, Ltd.

Patent 835120, which was sustained in the U. S. Supreme Court largely on the basis of an erroneous theory that the physical phenomena involved passed through a critical point as the quantity of oil was reduced, specified 1 per cent. by weight on the ore as its upper limit of operable oil quantity, and it was not until after many years of practice that the quantities of oil generally used got down to between 1 and 2 lb. per ton of ore.

The history of inorganic reagents is the same. Sulfuric acid was generally used, in quantities ranging from as high as 100 lb. per ton of ore down so rarely less than 5 lb. per ton. Almost the entire list of cheap inorganic electrolytes has been suggested and tried. Early practice tended toward acid and neutral compounds while present-day practice employs alkaline compounds predominantly, and the quantities rarely exceed 5 lb. per ton of ore.

In 1910, U. S. Patent 962678 for a soluble mineral-frothing agent was issued to Sulman, Greenway and Higgins, and companion patents were taken out in many other countries by the patent-holding corporation, Minerals Separation, Ltd., and its subsidiaries. On its face this patent was for use as the froth-producing agent in a particular type of froth flotation; *viz.*, the agitation-froth process,[2] of certain classes of water-soluble organic compounds of which the specific examples of the patent were: "amyl acetate and other esters; phenol and its homologues; benzoic, valerianic and lactic acids; acetones and other ketones such as camphor."

The patent corporation, however, succeeded in convincing the courts of the Third Circuit that this Patent covered, in addition to the soluble organic compounds specifically listed or generically indicated, the water-soluble portions of the "oils" of patent 835120, on the theory, good for patent litigation but of no weight scientifically, that while oils floated sulfide minerals because they coated them, these soluble mineral-frothing agents must act in some different way because, being in solution, they could not coat. The quantity of soluble mineral-frothing agent to be used was not definitely specified in Patent 962678; actually amounts of the specific agents named, ranging from a fraction of a pound to upwards of 50 lb. per ton, were required, according to the ore and the reagent.

During the period from 1913, when froth flotation was first introduced in commercial operation in the United States, to 1921, when the Perkins patent, U. S. 1364304, was issued, there gradually developed a realization among operators and experimenters that the organic flotation agents played a twofold part; *viz.*, that they, on the one hand, effected a segregation or "collection" of valuable mineral from gangue, and, on the other, affected the properties of the pulp water in such a way as to promote froth formation. In line with this understanding of their functions, a

[2] A. F. Taggart: *Op. cit.*, 796.

workable classification of organic flotation agents into "collectors" and "frothers" had developed in both operating and experimental terminology. Perkins, as the result of a masterly campaign of laboratory experiment, definitely segregated the frothing and collecting functions and discovered—and, in Patent 1364304, described—the new and highly effective type of collecting agent which is almost universally used today, and he pointed out the chemical characteristics upon which their action depends. The xanthates, thioureas, thioalcohols, diazo and amino compounds are typical examples of this class.

Perkins and his coworkers also found that the typical water-soluble organic collecting agents function best in pulps that are neutral or slightly alkaline, and while the possibility of treating certain ores in such pulps with oils had already been discovered, substantially universal discontinuance of acid pulps has now taken place, with resulting large economies in mill operation.

In the early work with flotation practically all of the sulfide minerals in an ore were floated alike, zinc with lead, iron with zinc or with copper, zinc with copper, etc. Many attempts at differential flotation of the sulfides are recorded in patent literature, most of them depending on the introduction of some reagent, in addition to the collecting and frothing agents, which was intended to have the power either to retard flotation of one of the sulfides or to accelerate flotation of the other. Practical and relatively universal solution of the problem did not come until the disclosure in 1922 by Sheridan and Griswold (U. S. Patents 1421585 and 1427235) that minute amounts of metallic cyanides caused marked lessening of the floatability of zinc and iron sulfides with respect to those of copper and lead. This discovery has completely changed the aspect of the zinc and lead markets of the world by changing a great number of substantially worthless deposits of complex lead-zinc-iron sulfides into valuable ores. The effect on copper has been less striking but is only slightly less important economically.

No such impressive record of achievement exists in the treatment of oxidized sulfide ores and of other non-sulfide ores by flotation, but such commercial work as has been done by sulfidizing oxidized sulfide surfaces and then floating, the laboratory work published by Gaudin, Glover, Hansen and Orr[3], and some of the experimental work set forth in the present paper indicate that an economical solution depends only on application of facts and principles already known.

## I. Collecting Agents

The preceding section sets forth what purport to be three different classes of reagents that effect collection of sulfide minerals: (1) oils, (2)

[3] Dept. of Min. and Met. Research, University of Utah, *Tech. Paper* No. 1.

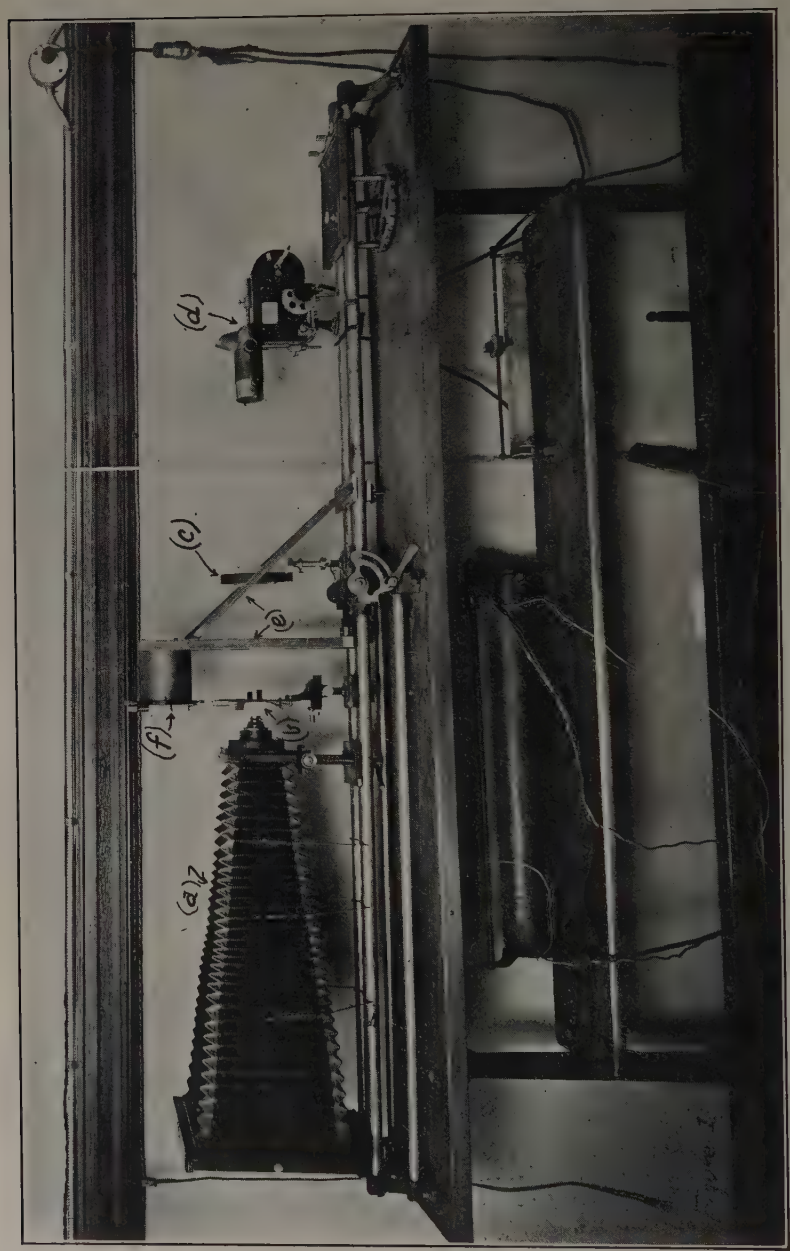


Fig. 1.—Bubble machine.

soluble organic compounds that froth, (3) soluble organic compounds that do not froth.

As a first step in developing possible differences the following "captive-bubble test" was devised for quantifying collecting effect.

Fig. 2.

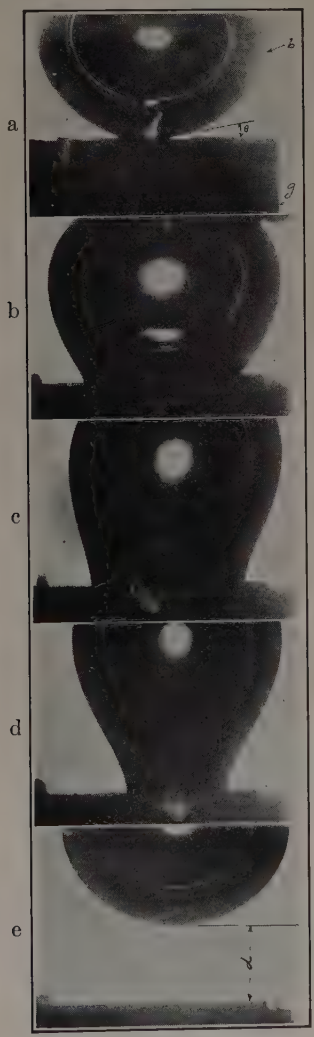


Fig. 3.

Fig. 2.—Longitudinal section of bubble holder. All transverse sections are circles. (Full size.)

Fig. 3.—Stages in investigation of a good collector.

*a.* Bubble just after being brought into contact with a particle of galena in distilled water.

*b.* Bubble in contact with same particle in $\frac{1}{40,000}$ potassium xanthate.

*c.* Distortion of bubble when holder is backed away unit distance.

*d.* Distortion of bubble when holder is withdrawn twice unit distance.

*e.* Relative positions of captive bubble and particle just after rupture; *i. e.*, position for "distortion" measurement.

*Captive-bubble Test*

In the trial of Minerals Separation, Ltd. *vs.* Miami Copper Co., W. M. Grosvenor performed an experiment in which bubbles, held captive in the bulb of a small thistle tube inverted under water, were used in attempts to pick up small mineral particles. This idea, amplified into the apparatus herein called the "bubble machine," gives a semiquantitative measure of collecting effect.

The bubble machine (Fig. 1) consists essentially of a camera *a* so set as to record on ground glass or a photographic plate the performance at a particle surface of a captive air bubble when both particle and bubble are immersed in a liquid in container *b*. This container is a plate-glass cell 2½ by 2½ by ⅜ in. inside, illuminated through the condensing lens *c* by the arc lamp *d*. The frame *e* carries a two-way vernier plate *f*[4] to which is attached a bubble holder (Fig. 2). This is made of glass, with inside diameter of the bubble cup *A* 2 to 4 mm., and is so held as to project down into the cell *b*, in the upright position shown in Fig. 2.

Operation of the bubble machine consists in filling the cell with the liquid whose collecting effect is to be tested, placing therein on the bottom of the cell the particle to be tested, immersing the cup of the bubble holder just below the surface of the liquid, and forming therein a bubble of the desired size by means of a curved medicine dropper, then, by means of the vernier screws, bringing the bubble down until the lower surface just makes contact with the upper surface of the particle, at the same time watching the operation on the ground glass of the camera. If collection is poor, there is little or no displacement of liquid from the particle surface by the bubble; if a good collector is present, the bubble spreads vigorously at the particle surface, displacing the liquid, until a position of equilibrium is reached at which the air-liquid contact apparently makes a definite angle with the liquid-solid contact surface adjacent. Fig. 3 gives photographs taken at several stages in the investigation of a good collector. Since the ability of the bubble to attach to and raise the particle is a function (1) of the ease with which the air of the bubble displaces liquid from the solid surface and (2) of the direction in which the pull of the bubble (due to its buoyancy) is exerted, the magnitude of the contact angle is one measure of the collecting effect of the liquid in which particle and bubble are immersed. This angle ($\theta$, Fig. 3*a*) is, therefore, measured on the projection of the image on the ground glass (or on the photograph). The bubble holder is then backed upward by means of the vernier, when the buoyancy of the bubble causes it to tend to rise, while at the same time it remains attached to the particle. If, as is normally the case, the particle is too heavy to be lifted by the bubble, the latter is deformed (Figs. 3*c*, *d*) and deformation con-

[4] This was actually a mechanical stage from one of the laboratory microscopes.

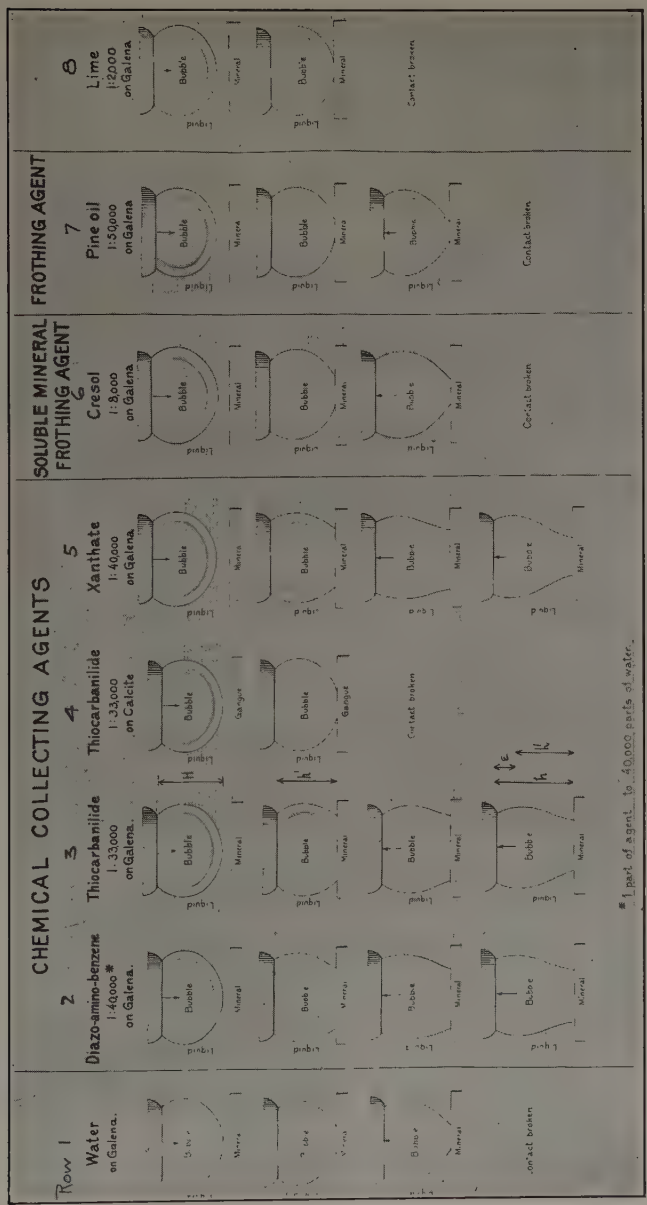


FIG. 4.—TESTS OF COLLECTING POWER.

Line 1.—Bubble approaching solid particle.
Line 2.—Bubble at instant of contact with solid particle.
Line 3.—Distortion of bubble after withdrawal of bubble holder through unit distance.
Line 4.—Distortion of bubble after withdrawal of bubble holder through twice the unit distance.

tinues until the bubble pulls away from the particle surface and assumes the position shown in Fig. 3*e*. Fig. 4 is from a tracing from a number of series of photographs such as are shown in Fig. 3. In this figure the distance *e* represents the deformation that the bubble has suffered before rupture of the contact, and since, for bubbles of the same size, this deformation is proportional to the pull exerted by the bubble, its magnitude affords another measure of collecting effect. Dividing the measured distortion *e* by the diameter of the bubble eliminates the effect of bubble size and gives a ratio, herein called "distortion ratio." Since it is difficult to get mineral particles so clean that they show no tendency at all to attach to air bubbles, the contact angle and distortion ratio were always first taken with all test pieces in distilled water before treatment with the solution and these figures deducted from the corresponding figures for the observation with the reagent. The arithmetical average of the net contact angle and net distortion ratio (the latter multiplied by 100 to make it of the same order of magnitude as the contact angle measured in degrees) is called herein the "collecting index."

Fig. 3 shows two sets of photographs from which the measurements necessary to calculate the collecting index for a 1/40,000 solution of potassium xanthate (one part xanthate to 40,000 parts of water) were taken. Fig. 3*a* shows the bubble *b* just after being brought into contact with a piece of galena *g* in distilled water. The contact angle $\theta$ is indicated. Fig. 3*b* shows the position taken by a bubble brought into contact with the same galena surface, but this time in a solution of 1/40,000 potassium xanthate. Fig. 3*c* shows the way in which the bubble becomes distorted when the holder is backed away a unit distance (1 cm. on the scale of the original photograph). Fig. 3*d* shows the distortion after withdrawal of the bubble holder through twice the unit distance. Fig. 3*e* shows the relative positions of captive bubble and particle just after rupture and gives the position for the "distortion" measurement. The distance *d* is the "distortion," and this distance divided by the bubble height *H*, Fig. 4, line 1, row 3, is the "distortion ratio." The contact angle in Fig. 3*a* is 15°, and in Fig. 3*b*, 60°, giving an increase in contact angle due to the reagent of 45°. The distortion for the bubble in distilled water on galena was 1.45 cm., the bubble height, 9.6 cm., and the distortion ratio, 0.15. The corresponding ratio for Fig. 3*e* is 0.34, and the excess over the distilled-water blank, 0.19. Multiplying this difference by 100 to make the figure of the same order of magnitude as the difference in contact angles, and averaging with this difference gives 32 for the "collecting index" of potassium xanthate solution against galena.

Table 1 (p. 332) gives the relative collecting indices for a number of familiar flotation agents, recalculated on the basis of 100 as the index for 1/40,000 potassium xanthate solution.

*Coating with Oils*

The net contact angles, distortion ratios, and collecting indices for emulsions of a number of different oils are given in Table 1. The particles were treated by holding them in tweezers and shaking them back and forth for a period of five minutes below the surface of an emulsion of the oil of the indicated strength, then transferring to clean water for the bubble measurement.[5]

One of the slogans of the early flotation litigation was that the amount of oil necessary in the agitation-froth process was so minute that in the operation it disappeared from cognizance of the senses. While this showy generalization was not at the time strictly true, later developments of the process to the point where frothing was effected with less than 1 lb. of, say, pine oil per ton of ore produced a concentrate and tailing in which neither sight nor the senses of smell or taste, unless most acute, could detect any oil. But the method of microscopic investigation devised by Tucker and Head[6] shows that undissolved oil produces coatings on sulfide particles which are of such thickness in certain parts, at least, as to be readily visible at 100 to 200 magnifications. Fig. 5, showing sphalerite after agitation in an emulsion of one part pine oil in 8000 of water, is typical. The contour-like lines visible in some of the oil patches show up as bands of different colors by direct examination. Fig. 6 shows a pine-oil coating on galena (one part pine oil to 4000 of water) in which the oil patches are smaller. (The clear part of the photograph is the protected portion.) Many of the individual oil patches in this field show the characteristic color banding under higher magnification. Fig. 7 shows a small section of one of the lines in a finger print with the grease deposits so thick in parts of the picture as to appear like mountains. Fig. 4 contains a line reproduction of a captive-bubble test with a 1/50,000 emulsion of pine oil. The galena particle showed no microscopically visible oil coating. The relative collecting index for the emulsion was 0.

It would appear on the strength of these tests that the collecting action of oil requires the formation of films or coatings of oil on the surface of the mineral particles of such thickness as to be visible, in part at least, under the microscope at medium magnifications.[7]

---

[5] It has been established that the collecting index thus measured is the same, within the limits of experimental error, as when measured in the emulsion, and the observation is much easier to make in clear liquid.

[6] E. L. Tucker and R. E. Head: Effect on Cyanogen Compounds on Floatability of Pure Sulfide Minerals. *Trans.* (1926) **73,** 354. See also page 321 of this volume.

[7] The apparent contradiction to this conclusion presented by the fact that a certain amount of flotation can be effected with an emulsion of 1/50,000 pine oil, which, according to Fig. 4 shows no appreciable collecting power and forms no visible coatings, arises from the fact that the bubble machine is a somewhat more rigid test apparatus than a flotation machine that is frothing freely.

5

6

7

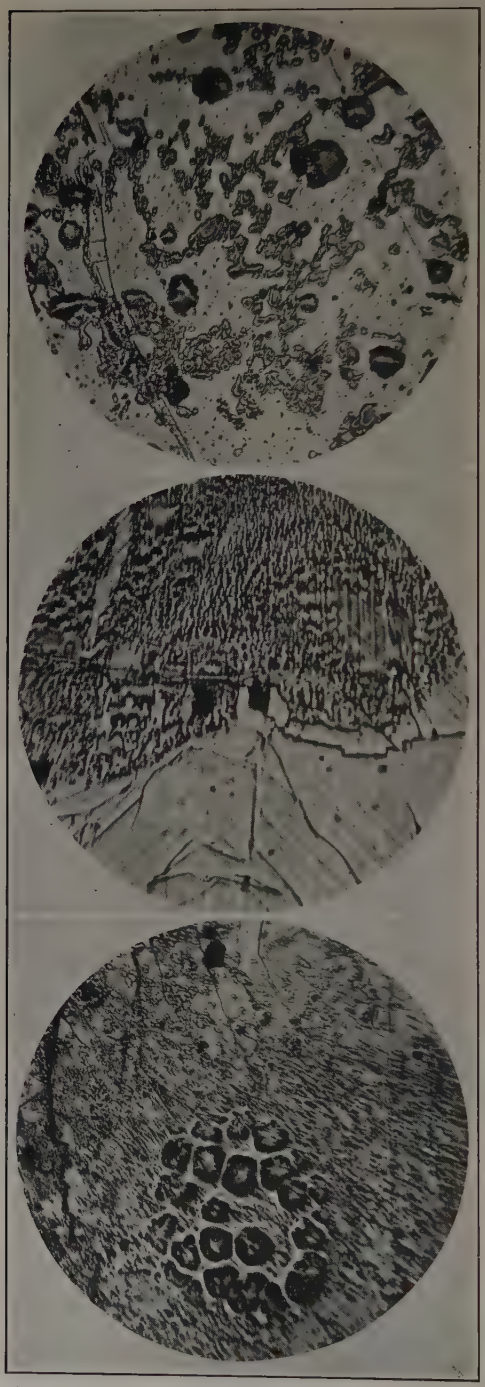

FIG. 5.—OIL COATING ON SPHALERITE PARTICLE.
FIG. 6.—PINE-OIL COATING ON GALENA PARTICLE.
FIG. 7.—SMALL SECTION OF ONE LINE IN A FINGER PRINT SHOWING GREASE DEPOSIT.

The explanation of the action of an oil coating in causing collection involves consideration of the solubility of the oil molecules, or the relative solubilities of different parts of them, in water, and perhaps also of the relative energies of the different interfaces involved, although it is not impossible that in several of the cases to be considered this latter factor should, properly, be merged in the first.

If we study first a system composed of galena, water and Nujol (a liquid paraffin [oil] as nearly insoluble in water as any liquid that

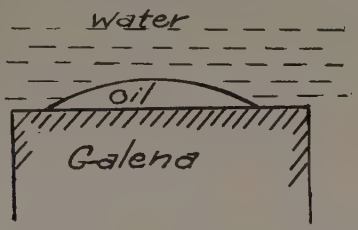


FIG. 8.—NUJOL IN CONTACT WITH GALENA PARTICLE IN DISTILLED WATER

the authors have been able to find), bringing a drop of the Nujol to a freshly cleaved and microscopically clean surface of galena in distilled water, the system assumes the position shown in Fig. 8. From the fact that the oil-galena interface increases at the expense of the water-galena interface, it follows, on the principle of least energy, that the surface energy per unit of area of the oil-galena interface is less than that of the water-galena interface. This conclusion is not, however, capable of

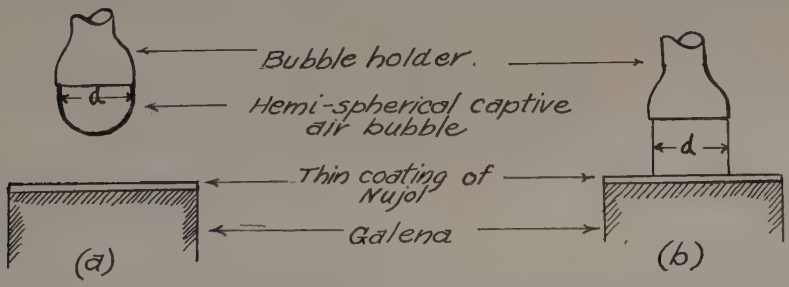


FIG. 9.—*a*. CAPTIVE AIR BUBBLE OUT OF CONTACT WITH OILED SURFACE. *b*. SYSTEM IN EQUILIBRIUM AFTER CONTACT.

direct proof on account of the impossibility, in the present state of knowledge, of measuring surface tension at solid-fluid interfaces. Consequently, although the conclusion is probably a correct one, it must be adopted with caution.

If, next, the Nujol is caused to form a thin film on a similar galena surface (by moving the galena particle around vigorously in a water emulsion of Nujol) and a captive air bubble (Fig. 9*a*) is brought into contact with the oiled surface, it spreads out thereon, displacing the water, until the system comes into equilibrium in some such position as

shown in Fig. 9*b*. In this case we are able to establish by independent proof—*i. e.*, surface-tension measurements—the explanation reached from the least-energy argument in connection with the Nujol-water-galena experiment above; *viz.*, that the surface tension of an air-Nujol interface is less than that of a water-Nujol interface and consequently the former increases at the expense of the latter until a condition of least energy is reached in the air-water-Nujol system. Thus the surface tensions, by the de Nuoy ring method,[8] of air-Nujol and water-Nujol interfaces are approximately 33 and 41 dynes per cm. respectively (room temperature).

An approximation of the energy drop involved when an air bubble spreads at a Nujol-water interface may be gained by applying known surface tensions to the surfaces pictured in Fig. 9. In 9*a* a captive bubble is pictured before coming into contact with the oil-coated galena; in 9*b* the bubble has been brought into contact with the galena and has spread out to a position shown in somewhat exaggerated form as cylindrical. (Actually the air-water-oil—on solid—contact angle, measured through the water, is 65° to 70° instead of 90° and the air volume between the bottom of the bubble holder and the oiled—solid—surface approximates a conical frustum more closely than it does a cylinder, but the approximate calculation is easier on the cylinder assumption, and the direction of difference is the same as in the actual case, though the magnitude of the difference in the actual case is not quite so great.) Since Nujol is insoluble in water it does not affect the surface tension of an air-water interface. Hence the total surface energy of the hemispherical air bubble at 9*a* is $\frac{\pi d^2}{2} \times 73 = 36.5\pi d^2$ ergs, where $d$ is in centimeters. The area of the cylindrical surface in 9*b* inclosing a volume equal to that of the hemisphere, is $\frac{\pi d^2}{3}$ and the air-water surface energy in *b* is $\frac{\pi d^2}{3} \times 73 = 24.3\pi d^2$ ergs. The air-oil surface energy in *b* is $\frac{\pi d^2}{4} \times 33 = 8.2\pi d^2$ ergs, and the water-oil surface energy of the area in *a* which in *b* is in contact with air is $\frac{\pi d^2}{4} \times 41 = 10.2\pi d^2$ ergs. The total energy of the system under consideration before contact (Fig. 9*a*) was, therefore, $36.5\pi d^2 + 10.2\pi d^2 = 46.7\pi d^2$ ergs; after contact (Fig. 9*b*), $24.3\pi d^2 + 8.2\pi d^2 = 32.5\pi d^2$ ergs. The difference, $14.2\pi d^2$ ergs, is proportional to the force which drives the readjustment.

Further confirmation of this reasoning lies in the fact that if an air bubble is brought into contact, under water, with a droplet of Nujol, it displaces water from a portion of the oil surface and the two bubbles, oil and air, stick together; but, since Nujol does not affect the surface tension

[8] *Jnl. Genl. Physiology*, **7**, 521.

of the air-water interface, the Nujol does not surround the bubble; *i. e.*, does not spread.[9]

These facts correlate plausibly with the hypothesis (which has considerable experimental support) that the surface energy of a liquid-liquid or gas-liquid (and probably of solid-liquid and solid-gas interfaces) is a function of the mutual miscibilities of the contacting phases. The surface tension of a liquid against its own vapor (as in a vacuum) decreases with increase in temperature to zero at the critical temperature. But the critical state represents the condition when the vapor tension is a maximum and movement of molecules across the gas-liquid boundary is most free. On the other hand, at low temperatures and low vapor tensions, movement of molecules through the bounding surface is sluggish and difficult and surface tension is high. In the case of a two-phase liquid system, if the contacting phases are but slightly miscible and readily saturated with each other, the condition corresponds to that of a liquid at low temperature and the interfacial tension is usually fairly high; with high mutual solubility and consequent freedom of molecular movement through the interface, conditions correspond to those in a liquid at elevated temperature and the interfacial tension is correspondingly low.

If this correlation is accepted, it is possible to think of the behavior of the captive bubble in terms of the solubility of the oil in the water and say that the reason that air displaces water from the oil surface is due to the reluctance of the oil molecules to become or remain surrounded by or in contact with water when opportunity is presented for them to escape this contact. This method of thinking is of great aid throughout in considering the phenomena of collection.

If, in the experiment pictured in Fig. 9, oleic acid is substituted for Nujol, it acts in the same way throughout except that when a bubble is presented under water to a drop of oleic acid, there is no tendency for the bubble to spread out; on the contrary, some of the acid leaves the mass and surrounds the bubble.

This difference in action is due to differences in the chemical character of the molecules. Liquid paraffin is a mixture of compounds of the general formula $C_nH_{2n+2}$ where $n$ ranges from 10 to 14. The structural formula is

```
  H  H  H        H  H  H  H
H C—C—C ......... C—C—C—C H,
  H  H  H        H  H  H  H
```

[9] Care must be taken in performing this experiment to have all of the entering constituents rigorously clean, and free of soluble organic materials, since these frequently are capable of dissolving in the oil and causing it to lower the air-water surface tension and therefore spread at this interface; *i. e.*, surround the bubble. The bubble-machine apparatus is ideal for following this phenomenon.

the dotted line representing suitable repetition of $\begin{matrix} H \\ C \\ H \end{matrix}$ to make up the requisite number of carbon and hydrogen atoms. The actual structure of the molecule is not, of course, correctly represented by this symbol, but no considerable violence to the facts will be done by visualizing the molecule as of some such general configuration, although in three dimensions. The molecular formula for oleic acid is $C_{17}H_{33}.COOH$ and the structural formula is

```
  H  H  H  H  H  H  H  H  H  H  H
H C—C—C—C—C—C—C—C =C—C···C—COOH.
  H  H  H  H  H  H  H     *  H  H
```

Disregarding the double bond (marked with * and coming between carbon 8 and carbon 9), which has no significant part in the present reasoning, this molecule may likewise be pictured as having some such general configuration as that of its structural formula representation,

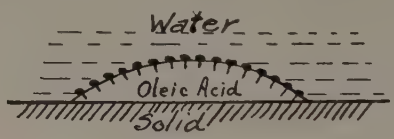


Fig. 10.

or perhaps more concretely as like a match stick in general outline,[10] the stick part made up of the $CH_n$ (hydrocarbon) groups and the head representing the COOH group (called carboxyl). These two parts of the molecule differ greatly in their solubility in water, the hydrocarbons being substantially insoluble and the carboxyl highly soluble.[11]

With these differences between Nujol and oleic acid in mind, the difference in behavior of the two oils in the bubble experiment is readily explained. The Nujol molecule as a whole, being insoluble in water, tended to get away from the water, but at the surface of the blob of oleic acid (the oil of Fig. 8) the molecules have all oriented themselves so as to have the carboxyl toward the water and the hydrocarbon, therefore, away (Fig. 10), since thus they at once satisfy the solubility tendencies in water of the two parts of the molecule. When the air bubble is presented (Fig. 11), however, since the solubility tendencies are further satisfied by spreading of the oil around the bubble, such spreading occurs. But there is no tendency for the bubble to spread out and displace water from the oil surface.

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[10] I. Langmuir: Constitution and Fundamental Properties of Liquids. *Jnl.* Amer. Chem. Soc. (1917) **39,** 1848.

[11] For further development of this thesis see page 312.

When, however, oleic acid is smeared in a very thin film on to a mineral surface, the molecules in the thinnest or monomolecular part of the film orient with the carboxyl end toward the mineral. The experimental work and argument underlying this conclusion are as follows:

1. If the system shown in Fig. 8 is placed in a vacuum tank with horizontal plate-glass top arranged to permit examination at 30 to 50 magnifications, of the upper mineral and oil surfaces, then shortly after a vacuum is applied gas (air) bubbles precipitate around the periphery of the dot, slightly away from the visible oil. There is no precipitation either on the visible oil or on the mineral surface at a distance therefrom. Consequently, since attachment of bubbles by precipitation and by the mechanical means of the captive-bubble method are different phases of the same phenomenon, and since it has been proved independently that there is no such attachment by either method with clean surfaces, we must

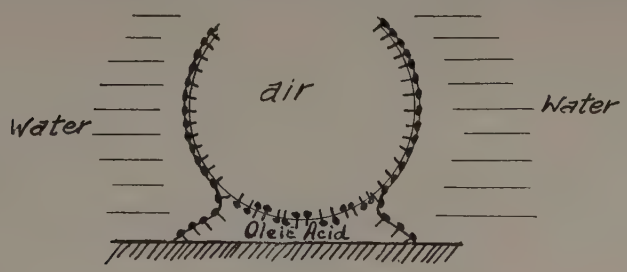



Fig. 11.

conclude that the visible oil of Fig. 8 is surrounded by a ring-shaped area of very thinly yet definitely oil-filmed surface.

2. If a clean water surface is carefully filmed, one molecule deep[12] with oleic acid, the orientation of the oleic acid molecules with respect to the air and water will be as shown in Fig. 11. If a piece of clean platinum, on which no air will precipitate under water, is placed down through the oil-filmed water surface, and a vacuum is applied, no air will precipitate, and the area of oil-filmed water will remain the same. This indicates that there has been no oil-filming of the platinum, both by the fact that the air failed to precipitate and by the further fact that there is no diminution in the area of water-surface contamination.

If, however, the clean platinum is placed in clean water, a monomolecular layer of oleic acid formed on the surface of the water, the platinum brought up through this surface into the air and allowed to drain, and then placed in clean water, gas precipitation occurs on the platinum surface when external pressure is reduced; *i. e.*, the platinum is now oil-filmed.

Looking again at Fig. 11, it will be clear that when the platinum passes from air into water the platinum surface is presented to the hydrocarbon

[12] I. Langmuir: *Op. cit.*

ends of the oleic-acid molecules, while when passing from water into air it is presented to the carboxyl end. Since oil-coating occurs in the second case, it would appear that in this system contact of carboxyl with platinum is essential to adhesion, in which case, after adhesion, hydrocarbon is presented to the water. If we can reason from platinum to galena, and there is no apparent objection, the thin invisible film of oleic acid surrounding the visible droplet in Fig. 8 is oriented with the water-repelling hydrocarbon end toward the water, and when a bubble is brought up to this it displaces the water, just as in the case of Nujol. Under such circumstances, air bubbles displace water from oiled mineral surfaces and adhere to them, which is the essence of collection.

Adhesion between a monomolecular film of oleic acid and a base-metal particle has commonly been attributed to adsorption; *i. e.*, to the fact that the interface water-solid has a higher energy per unit of surface than the sum of the energies solid-oil and oil-water. But, since neither of the solid-surface tensions can be determined, this "explanation" is nothing more than a statement that, if this were an adsorption phenomenon, this relation between surface tensions must be true, according to the Law of Least Energy. The latter is quite a different statement from the former.

It is not at all improbable that this particular coating phenomenon is of the same nature as that with the sulfhydrate type of soluble collecting agents, described on page 303, and that there is chemical reaction of the double-decomposition type between a soluble salt or base, developed at the surface of the metallic particles, and the organic acid.

### *Action of Dissolved Collecting Agents*

When we consider soluble collecting agents, the mechanism of the collecting phenomenon is harder to visualize than with oils, although the action of the agent at the sulfide surface is easier to describe in established scientific terminology.

Flotation procedure with soluble collecting agents is similar to the old procedure with oils, except that it is unnecessary to agitate the pulp as vigorously as is necessary with oil to coat the mineral particles. Simple immersion in a solution of one of the soluble collecting agents changes markedly the reaction of a sulfide particle toward bubbles, and this changed condition survives removal of the sulfide to fresh water in just the same way that the effect persists with oils. But there is no change in the sulfide surface, provided that it was originally clean and bright; that is, to any extent detectable either visually or photographically, even with the highest powered microscopes. On the other hand, analysis proves marked removal of collecting agent by the sulfide, and suitable experiment further proves that the material taken out is either the collecting agent as such or in an analogous chemical form readily transformed back to the original compound or to one closely allied thereto.

The discoverer of the soluble collecting agents (C. L. Perkins, U. S. Patent 1364304) sets forth their essential chemical and physical characteristics as follows:

1. Organic.
2. Slightly soluble in water.
3. Chemically reduced and easily oxidizable.

He specifies further that they should be nonoleaginous and nonfrothing, which are important characteristics from a practical flotation standpoint as well as from a legal point of view, but are not vital scientifically. The reagents named in the patent writing all contained either sulfur or nitrogen or both, and the action of the named reagents, as will be seen later, is dependent on these particular constituents, but collecting agents of similar action not containing either of these elements are embraced within the field of chemically reduced and easily oxidizable organic compounds slightly soluble in water, so that the presence of these elements is not necessary in this type of reagent.

The experimental work and argument that follow will be most readily understood, perhaps, if the conclusion to which they lead is first set down, as follows:

Soluble organic collecting agents function by reacting chemically with the surface substance of the mineral particle to be collected, thereby forming an organic reaction product that is insoluble in water in the concentration present, and adheres at the reacting surface and thereby changes that surface, for all practical purposes, to an organic surface with water-repelling properties.

That cementation of the molecules of collecting agent to the mineral particles is dependent on one part of the molecule, water repellency to another part, and that the active molecules are oriented, are proved by the following set of experiments.

1. 500 g. of galena was ground in a laboratory pebble mill for 30 min. in 350 c.c. of an aqueous solution of thiocarbanilid (see structural formula, Fig. 12) containing 63 mg. of the reagent (the grinding being approximately to all through 65-mesh); 79.4 per cent. of the thiocarbanilid was abstracted. Thiocarbanilid has a relative collecting index of 100.

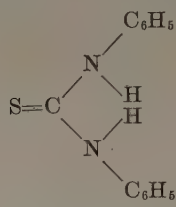
A corresponding test with carbanilid, the oxygen analog of thiocarbanilid (see Fig. 12), was attempted but on account of the very low solubility of this compound and the consequent uncertainty concerning the results, the investigation was turned to the monophenyl analogs.

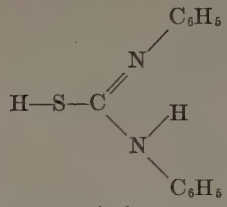
2. 500 g. of galena was similarly ground for 30 min. with 250 c.c. of an aqueous solution containing 18 mg. of monophenyl thiourea (Fig. 12). The solution, after the grinding, contained 3 mg. of the reagent, indicating 83 per cent. abstraction. (Relative collecting index, 59.)

3. In a parallel test with monophenyl urea (Fig. 12), 25 mg. went in and 23.2 mg. remained in solution, indicating 7.2 per cent. abstraction. (Relative collecting index, −6.)

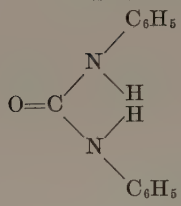
4. In a parallel test with thiourea (see Fig. 12), 62.5 mg. was added and 42 per cent. was abstracted by the galena. But the collecting index of thiourea is very low (5, Table 1 and Table 3 No. 453), which indicates that the coating has a depressing effect.

5. In a parallel test with urea (see Fig. 12), 61.6 mg. of the reagent added, there was no abstraction. Such a solution shows no useful collecting effect (see Table 3).

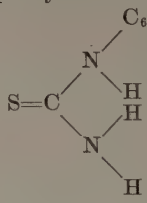




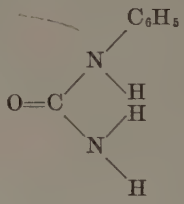
Thiocarbanilid (diphenyl thiourea), tautomeric forms.



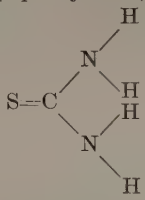
Carbanilid (diphenyl urea)



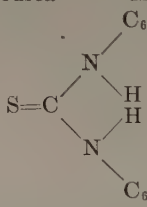
Monophenyl thiourea



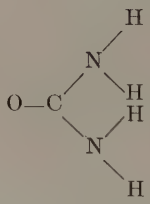
Monophenyl urea



Thiourea



Dioxyphenyl thiourea



Urea

FIG. 12.—STRUCTURAL FORMULAS, UREAS.

6. Dioxyphenyl thiourea (see Fig. 12) shows no collecting action in a flotation test (see Table 3, No. 209).

Comparison of paragraphs 2 and 4 with 3 and 5 shows that abstraction is a function of the sulfur group in the molecule; that when sulfur is replaced by oxygen, the remainder of the molecule remaining the same, abstraction fails.

Comparison of paragraphs 2 and 4 shows that water repulsion resides in the $C_6H_5$ groups; *i. e.*, while the reagent is abstracted in both cases,

it is only when the mineral coating thus formed contains this water-insoluble hydrocarbon group that collection is effected. Indeed, in the reverse case, when the part of the molecule not involved in the cementation is $NH_2$, as in paragraph 4, the flotation test cited indicates that the solubilizing $NH_2$ group renders the surface so water-avid as to make thiourea rate as a depressant.

It is true that there is nothing in the experimental work cited here that directly proves orientation of the abstracted molecules, but with abstraction localized in one part of the molecule and water repulsion in another part, with the molecule placed at the interface between visible water and solid, and with unsymmetricality in form a comparatively well-established fact respecting organic molecules,[13] the circumstantial evidence for orientation is strong. The fact cited in paragraph 5 also gives evidence on this point, although, lacking an abstraction test, it might be reasoned that the substitution of hydroxyl groups on the benzene ring had prevented mineral coating and that this was the reason for the failure of the dioxyphenyl thiourea to collect.

If thiocresol ($CH_3.C_6H_4.SH$) be taken as typical of one of the sulfhydrate class of soluble collecting agents, the following record of experiments is relatively convincing on the score of chemical reaction with the mineral to be floated:

1. Thiocresol (slightly soluble in water), if added to an aqueous solution of lead acetate or to an aqueous suspension of powdered lead carbonate or lead sulfate, reacts immediately to form a yellow precipitate of lead thiocresylate. With the sulfate the hydrogen-ion concentration increases and the filtrate gives a strong test for sulfate ion with barium chloride. These observed facts indicate a reaction of the type

$$PbSO_4 + 2HS.C_6H_4.CH_3 \rightarrow Pb(S.C_6H_4.CH_3)_2 + H_2SO_4$$

from the products of which we get: (*a*) rise in $H^+$ concentration by ionization of the sulfuric acid; (*b*) reaction between $H_2SO_4$ and $BaCl_2$ to give the characteristic white precipitate of barium sulfate; and (*c*) a water-repelling coating on the galena composed of the insoluble organic compound, lead thiocresylate. Quantitative work indicates that the reaction is not quite so simple as that set down, owing to the fact that the reacting lead compound is a basic sulfate rather than the simple sulfate, but otherwise the quantitative data confirm this hypothesis.

2. A crystal of cerussite (natural lead carbonate) soaked in a solution of thiocresol becomes covered with a yellow coating of lead thiocresylate but is not rendered readily attachable to bubbles. The reaction is

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[13] I. Langmuir: *Op. cit.*

R. W. G. Wyckoff: The Structure of Crystals. New York, 1924. Chem. Catalog Co.

W. H. Bragg and W. L. Bragg: X-rays and Crystal Structure. London, 1925 G. Bell & Sons, Ltd.

simple double decomposition of the type described in paragraph 1, but the coating is so thick that there is no orientation (see par. 5).

3. A crystal of galena soaked in thiocresol solution does not become visibly coated with lead thiocresylate, but its floatability (measured by the bubble machine) is markedly increased.

4. Powdered galena, shaken with a solution of thiocresol, causes marked abstraction of the thiocresol from solution, but there is no measurable increase in $S^{=}$ ion.

5. A cerussite crystal soaked in a solution of $H_2S$ turns black (by the formation of a skin of PbS) and this blackened surface will not attach to air bubbles. Neither addition of thiocresol to the $H_2S$ solution nor quick transfer of the sulfidized particle to thiocresol solution results in any enhancement of floatability in the bubble machine. But if the sulfidized particle is exposed to the air for a short time (5 min.) and then immersed in a distilled-water solution of thiocresol, the floatability, as gaged by the bubble machine, is high.

6. If galena powdered in air is shaken with distilled water, the hydrogen-ion concentration increases and sufficient sulfate ion goes into solution to give a precipitate with barium chloride and enough lead, also, for an unmistakable test.

7. When clean lump galena is ground in distilled water in an agate mortar or with silica pebbles in a porcelain mill, there is occasionally a faint odor of hydrogen sulfide,[14] the water becomes acid, and sulfate ion is present.

These various experimental phenomena harmonize with the conclusion that when galena is ground under oxidizing conditions the surface changes to a form of lead sulfate, which reacts with thiocresol to form an adherent coating of the relatively insoluble lead cresylate.[15] It is probable that the lead ions in the galena lattice are but little, if at all, displaced in the progressive steps of change of sulfide ion to sulfate and displacement of sulfate by cresylate, in which case the changed surface layer is held to the body of the particle by the same interatomic forces as those by which the original surface layer of lead sulfide was held. But this new surface layer, being made up of water-repelling (insoluble)

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[14] Mellor reports that in a sealed tube with air-free water at 150–200°, hydrogen sulphide is formed, the liquid becomes alkaline, and in some cases a red powder, possibly red lead, is formed. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, **7**, 789, New York, 1927. Longmans, Green & Co.

[15] The apparent contradiction in the citation from Mellor under paragraph No. 7 indicates that in the absence of oxygen the lead sulphide hydrolyzes to form $Pb(OH)_2$, a strong base, and $H_2S$, a weak acid. It is not impossible to conceive such a first step in the presence of oxygen, with subsequent oxidation of $S^{=}$ ion to $SO_4^{=}$ ion, but the extremely slow rate of oxidation of $H_2S$ to $H_2SO_4$ in standing solutions of the former and the rapid formation of $PbSO_4$ in washing precipitated PbS in analytical work favors the view that the action on PbS in flotation pulps is direct oxidation.

hydrocarbon groups ($CH_3.C_6H_4.S$) dries readily when exposed to air, which is to say that air bubbles attach to it readily.

A long list of organic compounds is known, having the general formula RSH, where R is a hydrocarbon group of relatively high molecular weight, all of which react with soluble base-metal compounds and thus produce coatings on sulfide particles that cause these to attach to air bubbles. Among the better known of these are thiocarbanilid, thiocresol and xanthic acid.

Alkali-metal xanthates are soluble collecting agents of the general type just discussed but differ from them in two particulars, *viz.*, (1) they are salts instead of hydrides, and (2) they are relatively soluble in water.

If we assume that galena is first exposed to water and then xanthate solution is added, the indicated sequence of reactions is:

1. Galena + water + oxygen react to form an adherent coating on the galena, thus: $Galena.PbSO_4.PbO_2.H_2O$. This reacts with xanthate as follows:

2. $Galena.PbSO_4.PbO.H_2O + 4K.SSCOC_2H_5 \rightarrow$
   $Galena.Pb(SSCOC_2H_5)_2.Pb(SSCOC_2H_5)_2 + 2KOH + K_2SO_4$

The conclusion indicated in the equations is supported by the following experimental facts:

1. Subsequent to placing the galena in water but prior to the addition of xanthate, there is a small but definite concentration of both $[Pb]^{++}$ and $[SO_4]^{=}$ ions in solution.

On addition of xanthate there occur

2. Abstraction of xanthate ion from solution.
3. Marked increase in concentration of $[OH]^{-}$ ion.
4. Marked increase in concentration of $[SO_4]^{=}$ ion.
5. No increase in concentration of $[Pb]^{++}$ ion.

The operating advantage of the alkali-metal xanthates over such a substance as thiocarbanilid lies in the greater solubility of the alkali salt and the consequent greater ease of dispersion through the pulp. The xanthate ion in combination with hydrogen (xanthic acid) is just as slightly soluble as thiocarbanilid and furthermore is distinctly unstable, tending to pass over into dixanthogen, which is distinctly inferior as a collecting agent.

Experimental proof that chemical reaction of the double-decomposition type is the basis of coating with collecting agents characterized by the presence of trivalent nitrogen is lacking. Sulfides abstract these compounds from solutions, and sulfides immersed in such solutions are thereby rendered readily attachable to air bubbles. These facts are readily proved. But we have as yet no series of simple tests, such as have been cited for the S-H compounds, to point experimentally to the conclusion that chemical reaction is the essential mechanism in the formation of the water-repelling surface on the sulfides.

Considering first the typical amino compounds, the weight of the evidence seems to be against assignment of the credit for oriented coating to acidic amino hydrogen, for the reason that a number of the tertiary amines are good collectors. Nevertheless the data prove conclusively that the forces causing removal of the amino compounds from solution are seated in the amino part of the molecule, as witness the relative performances (Table 3) of naphthol and naphthylamine, phenol and aniline, cresol and toluidin.

A similar line of reasoning with respect to azo and diazo compounds seats the collecting activity in the azo group, likewise trivalent nitrogen. Thus azobenzene and azonaphthalene are collectors (see Table 1) while benzophenone (see Table 3) is not a collector. (The rating of azobenzene and azonapthalene in Table 3 as noncollectors is due to failure to get them into solution, as was done with much difficulty in the work on which Table 1 is based.) Similarly diazo-amino-benzene ranks as a collector (Table 3) while benzanilid is a noncollector.

It is easy to say that the explanation of the observed abstraction of nitrogen-bearing collecting agents from solution and the resultant modification of sulfide surfaces is embraced in the word adsorption. But such an explanation is little more than a restatement of the fact, since the word adsorption means nothing more than concentration of a substance from solution or suspension at the interface between the dispersing medium and some other phase with which this medium is in contact. In a broad use of the term, the coating of sulfide by S-H compounds, such as thiocresol, is adsorption, although here the thiocresol molecule as a whole is not removed and a recognizable chemical reaction is the moving force in bringing about the result. In the case of the nitrogen-bearing collecting agents, it would be in accord with much of present-day speculation to credit an adsorption in which the motive force is due to the fact that the energy of the solution-solid system is reduced by concentration of the solute at the liquid-solid interface; in other words, to extend to the solution the same reasoning that has already been used in connection with oil-coating (p. 295). But such an explanation, in so far as it departs from the mere change in terminology involved in the introduction of the word adsorption, depends for verification upon the determination of solid-liquid surface tensions, and this, as has been previously stated, is not a possibility in the present state of knowledge.

It seems to the authors, therefore, that less violence is done to intellectual proprieties in proposing that the abstraction of the trivalent nitrogen compounds is due to forces that lie near to the field of well-recognized chemical interaction which proposal rests upon analogy with the established behavior of the sulfhydrate class of soluble collecting agents than in setting up an adsorption hypothesis by an attempted analogy between the action of individual molecules in solution and that of groups of millions of molecules in the form of droplets of undissolved oil.

## II. Frothing Agents

### *Quantification of Frothing Effect*

Frothing proved even more difficult to quantify than did collecting. After many trials the apparatus pictured diagrammatically in Fig. 13 was devised. The small frothing cylinder *a* was 2⅛ in. inside diameter by 9½ in. deep from blanket surface to overflow. Air pressure and, consequently, air volume passed through the blanket were regulated by varying the discharge through a ⅛-in. needle-type exhaust valve. The blanket was kept wet and was carefully cleaned with a strong water jet after each test, but it was found impossible to keep the volume of air discharged through the blanket at a given pressure constant from day to day or even from test to test and therefore the procedure described in the next paragraph was adopted.

With the cell clean and empty and with enough air coming through the blanket to prevent downward passage of water, 100 c.c. of the solution or emulsion to be tested was poured in and the air supply reduced to the point where just enough air came through the blanket to cover from half to three-quarters of the surface with a layer of bubbles one

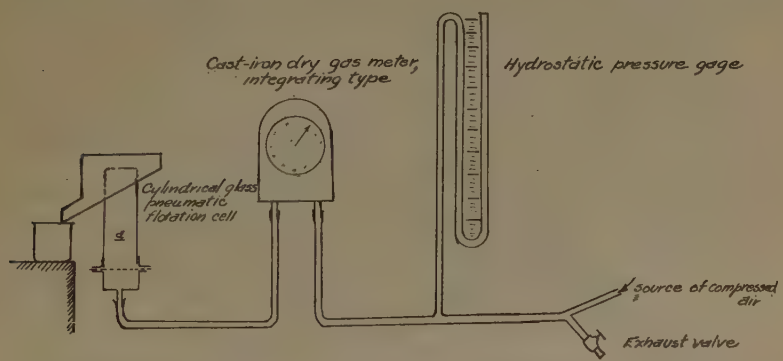



Fig. 13.—Apparatus for quantification of frothing effect.

bubble deep. Twenty-five grams of ore (dry-ground through 65-mesh) was then added, and the pressure brought up at the rate of 1 in. of water per 15 sec. until overflow started. Overflow was maintained for a period of 5 min. at as nearly as possible a constant rate, similar to the eye to the rate obtaining in normal laboratory testing procedure; pressure and meter readings were made, and the collected overflow was weighed wet and dry. The wet weight, expressed in grams of overflow per cubic foot of free air, gave a relative measure that was found to accord with qualitative experience and was, therefore, adopted as having semiquantitative significance.

### *Relation between Frothing Effect and Chemical Composition*

Table 2 shows the results of a number of frothing tests in the apparatus shown in Fig. 13, carried out by the method described. The figures for

pine oil, phenol and cresol are plotted in Figs. 14 to 16. These tests point to a number of interesting conclusions.

The pine oil tests (Fig. 14) show that within the range of concentrations commonly in use (1 lb. of reagent per ton of ore is equivalent to 125 mg. per l. in a pulp containing 20 per cent. solids) the percentage of solids in the overflow will tend to increase with decrease in quantity of the frothing agent. The probable explanation of this fact is that with the smaller frothing effect that goes with the lower quantity of oil more air is necessary to effect a given overflow. This results in a more powerful upward current in the cell which carries more solid up with the water. The result is a familiar one in the mill in the watery, lightly loaded froth that comes with a moderate amount of over oiling. The rise seen in the branch of the curve to the right of 120 mg. per l. is due to a modification

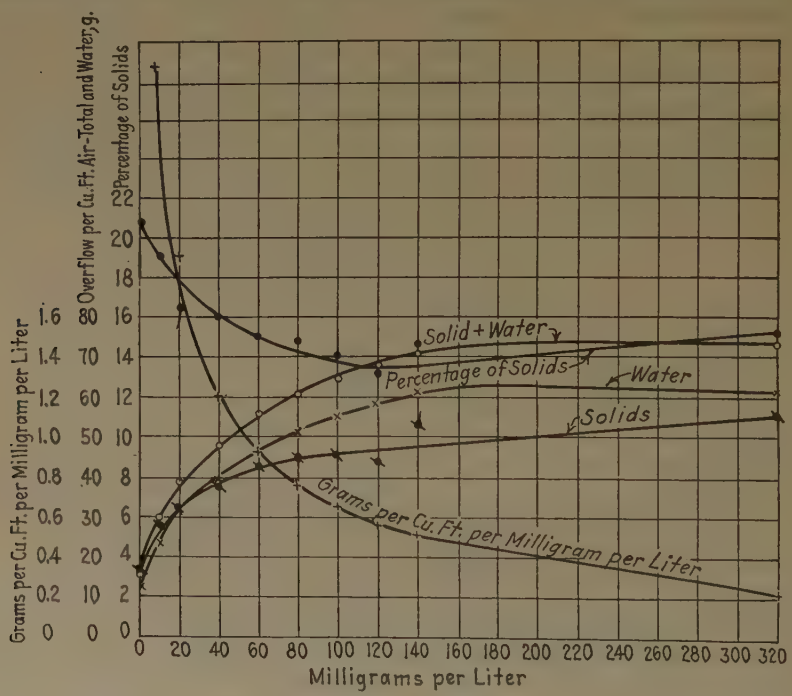



FIG. 14.—PINE-OIL FROTHING TESTS.

of the same cause that brought about the rise to the left. During the test with this large amount of oil it was observed that the entire volume of the cell was filled with bubbles of relatively small size. This made it difficult for solid matter to settle, and consequently more was carried over. This condition in the cell is the same that obtains when the cell is forced with a small quantity of frothing agent present.

The weights of solid matter and of water frothed over increase with increase in the concentration of pine oil, but at a decreasing rate. The rate of decrease in slope of the tangent to these curves is greater beyond

concentrations of 50 or 60 mg. per l. than would be the case in a larger cell on account of the fact that the experimental cell was a batch machine and with these higher concentrations the bulk of material in the cell diminishes so greatly toward the latter part of the test that the overflow rate is lessened on that account. There is, of course, nothing in this behavior not already well known in a general way to millmen. The curves do show, however, that if a relatively high concentration of frothing agent is already in use, little added frothing effect is to be expected from a relatively large increase in amount of reagent. This fact is accentuated with phenol (Fig. 16).

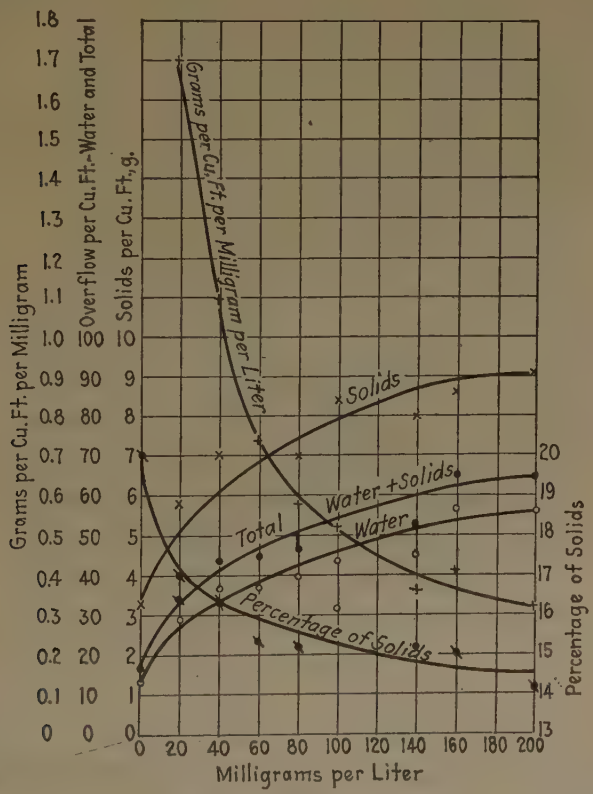



FIG. 15.—CRESOL FROTHING TESTS.

The curve labeled "Grams per cubic foot per milligram per liter" emphasizes the desirability, from an economic standpoint, of using a powerful frother which gives a large variation in frothing effect for a relatively small change in concentration.

The curves for cresol (Fig. 15) are similar in all respects to those for pine oil, but differ in the fact that the amount of overflow per cubic foot of air per milligram of reagent is less with cresol.

The curves for phenol (Fig. 16) differ from those for cresol and pine oil in three important particulars. In the first place, the three curves

showing quantity of overflow per cu. ft. of air per unit of concentration of reagent lie lower on the vertical scale than those for either of the others, indicating phenol a poorer frother. Next, the curve showing the relation between percentage of solids in the overflow and quantity of reagent present passes through a minimum at some place between 25 and 75 mg. per l. concentration and the percentages of solids are higher throughout than those for the other reagents. This is a result of the poorer frothing ability of the phenol and the physical explanation of the high solid content of the froth is the same as that given for the rises either side of the

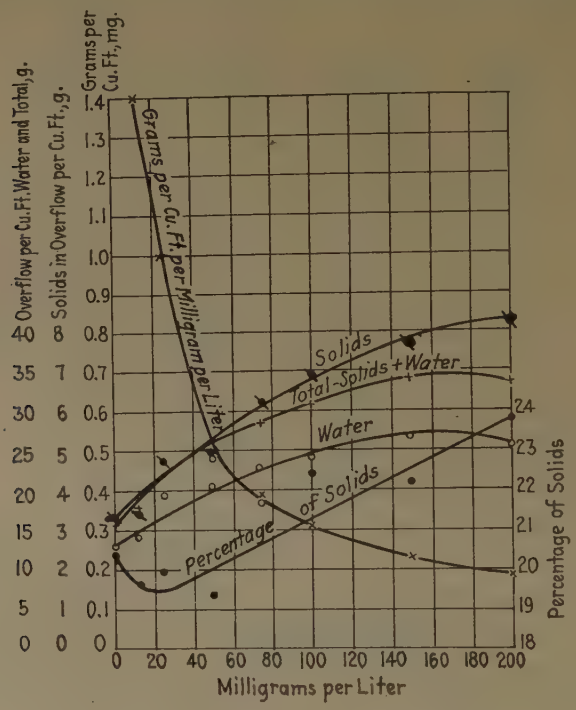



FIG. 16.—PHENOL FROTHING TESTS.

minimum of the pine-oil curve (p. 308). Finally, it is to be noted that the curve representing the weight of water overflowed per cubic foot of air per unit weight of reagent passes through a maximum in the higher ranges of concentration. This was forecast in the curves for pine oil, and is probably a characteristic frothing phenomenon.

An attempt was made to correlate the frothing effect of the pine-oil emulsions with the surface tension of the solutions. Surface-tension determinations were made with a de Nuoy ring balance on the emulsions used and on the supernatant liquids from the overflow and tailing from frothing tests. (Filtration of the products to obtain samples for surface-

tension testing gave results that were erratic and unreliable.) The results of a series of determinations are summarized in the curves of Fig. 17. The first noteworthy fact is that except at concentrations less than 20 mg. per l. the surface tension of the original bulk solution (emulsion) is less than that of either of the products, while on the established theory of froth formation it should fall between them. There are two

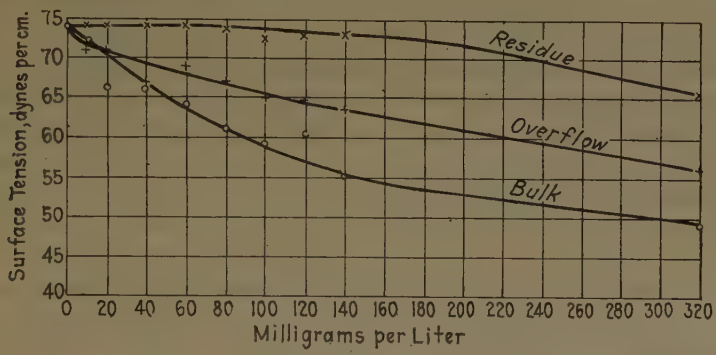



FIG. 17.—PINE-OIL SURFACE-TENSION TESTS.

obvious explanations of this discrepancy. In the first place there is considerable evaporation of pine oil in the course of a test. In the second place, the original emulsions of all but the most dilute mixtures contained a considerable amount of undissolved oil. Such oil concentrates by gravity at the surface of the original mixture but adheres to the solids in a frothing test and thereafter is ineffective to alter the surface

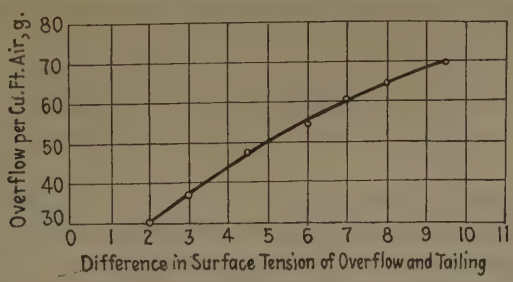



FIG. 18.—SURFACE TENSION VERSUS FROTHING WITH PINE OIL.

tension of either overflow or tailing water. This latter is undoubtedly the more important factor of the two discussed.

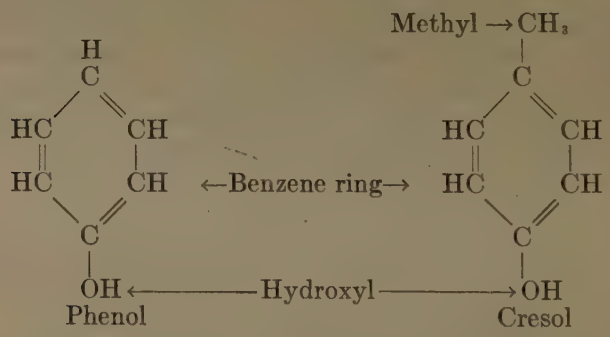
The curves show the overflow water to have a lower surface tension than that of the tailing water at all concentrations of pine oil, demonstrating, of course, concentration in the bubble films during frothing.[16]

[16] For demonstration of the fact that any frothing agent attached to the mineral particle stays there, and hence could have no effect in these measurements, see A. F. Taggart and A. M. Gaudin: Surface Tension and Adsorption Phenomena in Flotation. *Trans.* A. I. M. E. (1923) **68**, 479.

The surface tension of the tailing water, for all concentrations within the range of present-day practice, is practically that of pure water, showing substantially complete utilization of the soluble oil, at least, in frothing.

Fig. 18, which is derived from Figs. 17 and 14, shows the extreme importance in frothing of a reagent that causes great changes in surface tension for small changes in concentration. The increase in frothing effectiveness with difference in surface tension between overflow water and tailing water is practically a straight line throughout the usual concentration range. The fact that a concentration of pine oil of 20 mg. per l. is sufficient for effective flotation with a good nonfrothing collector, taken in connection with Fig. 17, shows that a surface-tension drop of 3 to 4 dynes per cm., if caused by a small quantity of reagent, is sufficient for effective frothing.

Table 2 forms the basis for an interesting generalization on the relation between chemical structure and frothing effect. As has already been noted, the frothing effect of cresol is greater than that of phenol. But structurally cresol is phenol with a methyl ($CH_3$) group replacing one of the hydrogens on the benzene ring.




In frothing, these unsymmetrical molecules pass into the air-water interface, orienting themselves with the water-avid hydroxyls in the water and the water-resisting $CH_n$ groups in the air. They thus lower the surface tension of the solution and, by reason of the fact that the change in surface tension is proportional to the concentration of hydrocarbon in the surface, make frothing possible. The readiness with which the molecules pass into the air-water interface and stay there is inversely proportional to the solubility of the hydrocarbon part, and this decreases with increase in hydrocarbon content. On the other hand, if hydrocarbon is loaded on until the solubility becomes very small, the difficulty in obtaining sufficient molecular dispersion becomes so great that the substance becomes impractical for flotation. Xylenol, naphthol and carvacrol (Table 3) are OH compounds of heavier hydrocarbon

loading than cresol and all are more vigorous frothers, but in cetyl alcohol the OH is so heavily loaded with hydrocarbon that sufficient molecular concentration cannot be obtained in the flotation pulp.

Aniline and toluidin are analogs of phenol and cresol respectively in which $NH_2$ replaces OH as the water-avid group, the remainder of the respective molecules being the same. Table 2 shows that these amino analogs are the less vigorous frothers. Xylidin is next in the amino series above toluidin and the order of increasing frothing effectiveness within the series is, from the table, aniline, toluidin, xylidin.

The comparison of effect of the hydroxyl and amino analogs brings out the fact that all water-avid groups have not the same effect. Amino is not so vigorous a solublizer as OH (compare the solubilities of aniline and phenol, toluidine and cresol given in Table 3), consequently the sharpness and rapidity of orientation of the amino-bearing molecules at the air-water interface are less.

This topic is considered further on page 317.

## Statistical Study of the Relation between Structure and Solubility of Organic Compounds and Their Function in Flotation

The most interesting and useful result, from a scientific standpoint, of the work done on the water-soluble flotation agents, following Perkins' discovery of soluble nonfrothing collecting agents, is the fact that we are now able to predict with relative certainty, knowing the structural formula and solubility of an organic compound, whether or not it will function as a frother or collector, which, and something as to its efficiency. Table 3 is made up from the list of substances tested by Perkins at the Mellon Institute of Industrial Research, University of Pittsburgh (*Monograph* of Metals Recovery Co. Industrial Fellowships Nos. 1, 2, 3, 4, 5, 6, 7 and Extension, Nov. 1921); three lists of substances tested by T. A. Janny and B. S. Morrow at the Utah Copper Co. and the Anaconda Copper Mining Co. respectively and published in Book of Exhibits, Vol. I, Record C. C. A. Ninth Circuit, Metals Recovery Co. *vs.* Anaconda Copper Mining Co.; and from tests made by the authors at Columbia University. In this table the chemicals tested are listed in alphabetical order, followed by the usual structural formulas. The solubilities are mostly from the Handbook of Chemistry and Physics, 11th ed., by C. D. Hodgman and N. A. Lange, Chemical Rubber Publishing Co., Cleveland, Ohio, 1926.

The numbers under the heading "Results of flotation test" are both positive (no sign), and negative (minus sign). A positive number shows the percentage increase in recovery over that obtainable by the use of frothing agent alone (pine oil), that the addition of the collecting agent effected, the denominator of the percentage fraction being the difference

between the percentage recovery effected with the frothing agent alone and 100. Thus if a test with pine oil alone gave 40 per cent. recovery and a parallel test with the same amount of pine oil plus a given collecting agent gave 60 per cent. recovery, the increase in recovery due to the collecting agent is 20 per cent. and this, divided by 60, the difference between the recovery in the original pine-oil test and 100, gives a figure of 33, which is that recorded in the table under the heading "Collecting." Similarly with the negative numbers, except that the divisor is the original pine-oil percentage recovery. The lower-case letters represent estimates by the experimenter, no assays being made. The column headed "Classification" carries the authors' estimates of the reagent, based on the flotation test, the order being frothing-collecting. Thus the first notation, F-C, signifies a frothing-collecting agent, the next O-O, nonfrothing, noncollecting; etc. The next column lists the polar groups; *i. e.*, those that are generally chemically active and water-avid, which, according to the theory herein developed, constitute one of the indexes of flotation activity. The last column gives the number of carbon atoms not attached to or forming part of a polar group (called "insoluble carbons").

Table 3 shows that out of the 493 reagents tested, 79 were nonfrothing collecting agents. Examination of the polar groups occurring in these 79 compounds shows the following percentage order of frequency: amino-nitrogen (N‴, NH, $NH_2$) 28.4; azo (N:N) and diazo (N:N.N) nitrogen, 11.3; divalent sulfur (S″), 11.2; thioamide (CSNH, $CSNH_2$), 8.6; hydroxyl (OH), 8.6; sulfhydrate, 8.0; and a scattering of others of which only one, CSeNH, is significant. In only 12.7 per cent. of the nonfrothing collectors are nitrogen and sulfur both absent. This fact so nearly justifies the conclusion that the presence of trivalent nitrogen or divalent sulfur is necessary in a reagent of this class as to warrant close scrutiny of the apparent exceptions. The first, chlornitrobenzene [p], forms an oily liquid when mixed with acid water; p-chlortoluene is an oily liquid, only slightly soluble in water, and used in the quantity of 1 lb. per ton, as was done in the tests recorded, may easily be excluded here as having acted as an oil. This exclusion is the more readily justified in view of the fact (p. 317) that the presence of halogen in a compound is generally distinctly detrimental to collecting action by dissolved chemical compounds. Ethyl nitrobenzoate [m] should probably have been classed as a frother, as was its para isomer, No. 232. Lauric acid is a greasy solid, of the general class of fatty acids of the oil patent 835120, and most of its collecting effect was probably due to mechanical greasing of the mineral-particle surfaces. This leaves as unexplained exceptions to the general rule iodoform, nitronaphthalene, nitroso [β] naphthol, trichlor benzene, and trinitrotoluene.

The average number of "insoluble carbons" in the molecules of the nonfrothing collecting agents of the table is 8.2; in 73 per cent. of the compounds of this class the carbon-oxygen ratio is 6 or greater; and in 79.5 per cent. the solubility is rated as "slight" or some lesser degree.

Of 114 reagents that rate as noncollecting frothers (F-O), 110 or 97.3 per cent. contain an oxygen-bearing polar group. The principal characteristic frothing groups, in the order of decreasing frequency of occurrence are OH (hydroxyl), CO (carbonyl), COOH (carboxyl), CONH (amide), COO (ester) and COC (ether). An amino group als occurs in many of the pure frothers, but in none is this the sole polar group.

The mean number of "insoluble carbons" in these 114 compounds is 5.5; only 34.5 per cent. have a carbon-oxygen ratio of 6 or greater; more than half of the compounds fall in the solubility groups "soluble" and "slightly soluble," with more than half of the remainder lying toward the less soluble side of this range.

Of 66 frothing-collecting agents (F-C), 28 contained an amino group as the only polar group. This is entirely sufficient to establish the amino grouping as capable, in proper combinations, of froth production as well as mineral collection (p. 313). In 9 out of the 66 compounds, the only polar group was one in which oxygen was linked with carbon. This is the grouping that predominates in the pure frothers and the one characteristic of the compounds listed in Patent 962678 (p. 286). Thirteen of the 66 carry both carbon-oxygen groups and amino groups, and their combined frothing and collecting power is precisely what is to be expected from the statistical analysis of the nonfrothing collecting and noncollecting frothing groups. The other 25 compounds carry a diversity of polar groups. Nos. 57, 58, 205, 232, 330 to 333 and 345 are characterized by a nitrogen-oxygen linking, which is sufficient to explain their frothing characteristics. Nos. 57, 58 and 333 are liquids of slight solubility used in quantities sufficient to effect collection by mechanical smearing. The others are, however, nongreasy solids and their collecting effect is not to be explained on the ground of mechanical smearing. For the present they may be added to the two similar compounds (Nos. 339 and 472) occurring in the nonfrothing collecting classification, as indicative of the conclusion that nitrogen-oxygen groups in certain combinations have collecting power. No. 327 carrying nitro ($NO_2$) and amino groups needs no further comment. The cyanide group ($C{\equiv}N$) in No. 110 is highly water-soluble, which explains its frothing effect, and at the same time contains trivalent nitrogen, which is characteristic of the collecting groups. In Nos. 216, 363, 366 and 445 collection may be attributed to the sulfide sulfur ($S''$) and frothing (and possibly some collection) to the amino group.

There remains to consider four reagents in this group; *viz.*, Nos. 112, 125, 126 and 480. These contain sulfhydrate and sulfide sulfur as the

only polar groups and these are distinctly characteristic of nonfrothing collection. Whether the frothing effect attributed to them in the table is due to experimental inaccuracy or impurity of the samples, or is characteristic of the groups in certain combinations, the authors are not as yet able to say. Certain it is that in the majority of tests carried out in the Columbia University laboratory, using amounts of this type of reagent amply sufficient for good collection, there was no sensible amount of frothing.

The mean number of "insoluble carbons" in the 66 frothing-collecting agents is 6.6; 67 per cent. have a carbon-oxygen ratio greater than 6; 71 per cent. fall into the solubility groups rated "slight" or less.

The nonfrothing noncollectors number 197 individuals. The five most frequently appearing polar groups are: amino ($NR_3$), 19.4 per cent.; hydroxyl (OH), 14.3 per cent.; amide (CONR), 10.7 per cent.; carboxyl (COOH), 8.4 per cent.; and carbonyl (CO), 6.5 per cent. The high frequencies of the hydroxyl, carboxyl and carbonyl groups have no significance other than that, with hydrocarbons substantially excluded by former experience, the oxygen groups necessarily rank high in any random selection from the remaining list of organic chemicals. The high frequency of amino groups is explained by the fact that all three experimenters consciously favored the inclusion of nitrogen-bearing compounds in their lists of substances to be tested because of prior knowledge of the probable efficiency of such compounds, but without understanding of the fact that the relation of the amino group to the remainder of the molecule, the character of the remainder of the molecule and the solubility of the substance were also important factors.

The high rating of the amide group in this class is, however, significant, particularly when considered in connection with its frequency in the other classes. It forms 1.8 per cent. of the polar groups in the frothing collectors, 2 per cent. in the nonfrothing collectors, and 11.5 per cent. in the pure frothers (F-O). Clearly, then, this group, in proper combination with "insoluble carbons," is froth producing, but the collecting property ordinarily associated with trivalent nitrogen is in some way inhibited by the close association with carbonyl.

It is clear from study of the compounds in this class that the presence of a given polar group, which in certain combinations may be shown definitely to be responsible for a useful flotation effect, is not in and of itself any assurance that the compound will function.

An analysis follows of the characteristics of this inert (O-O) class into groups that experience, prevalence, etc., might lead one to hold as indications or causes of non-success:

*Solubility.*—"Very soluble" or greater, 28.7 per cent.; insoluble, 26.7 per cent. If a compound is very soluble, it usually means such a low carbon content that even if it coats the mineral it will not turn

water therefrom, and its frothing capacity is small because there is no force to drive it into the air-water interface; if insoluble, it cannot act as a frother, nor, unless as an oil, as a collector.

*Low "Insoluble-carbon" Count.*—In 30.6 per cent. of the substances in the inert group the "insoluble-carbon" count was zero or one. This normally connotes a solubility rating of "very soluble" or "infinite," but even where this is not the case, the important orienting influence of the "insoluble carbon" part of the molecule is missing, and this, as has been previously developed, is an essential part of the molecule in successful flotation service.

*Halogens.*—In 5.6 per cent. of the members in this class what may be called "active halogen" occurs; *i. e.*, nonionized halogen in combination with some other group that renders the halogen soluble or active chemically. Judging from the comparative absence of halogen polar groups in the frothing and collecting classes, the empirical conclusion that they inhibit collection and do not aid frothing seems to be justified.

*Sulfate sulfur* does not occur among the polar groups in either of the collecting classes, against 6 occurrences out of 197 individuals in the inert class and 5 out of 71 in the depressing classes (O-D, F-D). This seems to be sufficient basis for the empirical conclusion that the sulfate sulfur group inhibits collection.

Certain of the failures furnish excellent confirmation of the general theory. Thus No. 209, dioxyphenylthiourea, is thiocarbanilid, a good nonfrothing collector, with OH, a solubilizing radical, substituted on the water-repelling ends and these being no longer water-repellent, the compound fails as a collector. Hydroxyazobenzene is the same as aminoazobenzene, except that OH is substituted for $NH_2$. But this constitutes elimination of the group in which an important part of the activity of the aminoazobenzene appears to reside, hence the failure to function. No. 346 is toluidin, a frothing collector, with the solubilizing $NO_2$ group inserted on the water-repelling end of the molecule. No. 450 is an S-H compound, but has only one hydrocarbon or water-repelling unit, and has in addition the solubilizing COOH group. Nos. 487 and 488 are especially interesting in that the acidic hydrogen of xanthic acid has been replaced by $-C_nH_{2n}.COOH$, and as a result the acidic hydrogen of the compounds is now part of a carboxyl group, and the collecting ability of the compound is on a par with that of other COOH compounds; *i. e.*, substantially nil.

The mean number of "insoluble carbons" in these O-O compounds is 5.7; 52 per cent. of the carbon-oxygen ratios are less than 6.

Twenty-nine of the reagents of Table 3 rank as nonfrothing depressing agents (O-D); *i. e.*, when added with pine oil in the tests they lowered the recovery below that obtainable with pine oil alone. These compounds fall into no predominant structural classifications that would

explain their depressing action, but albumen, amygdalin, dextrin, gelatin, inulin and tannic acid form colloidal solutions; eosine is a fluorescing dye, indicating colloidal suspension; and ammonium eosine, which is the ammonium salt of eosine, probably decomposes to eosine in acid and neutral solutions (it was not a depressant in alkaline solution). Experiments with two other colloidal substances point to a probable explanation of the action of all.

(1) A bubble test with galena in saponin solution (saponin is a glucoside like amygdalin) showed that the bubble could not be made to attach itself to the galena particle even when forced down on to it so hard as to displace the bubble from the holder.

(2) Galena, which is readily attacked in warm potassium dichromate solution and coated with lead dichromate, is protected from all action of the dichromate if a small amount of glue is present in the solution.

These two experiments indicate that, so far as the colloids are concerned, the depressing action is due to coating of the sulfide particle by the colloidal suspension and that this coating vigorously opposes bubble attachment. Pyrogallic acid reacts rapidly with iron salts in solution to form a colloidal suspension and also to form a visible coating on sulfides that completely prevents bubble attachment in the bubble machine. Pyrocatechin reacts similarly with iron salts. Galactose and maltose are sugars and their solutions probably act in somewhat the same way as the colloidal solutions, although we have no direct evidence on this score.

Numbers 13, 62, 63, 72, 166 and 418 are complex organic salts carrying strong solublizing groups and if they attach themselves to the mineral particles, these groups would produce a water-avid rather than a water-repelling surface. The formation of such a water-avid surface is probably the explanation of the depressing action of aminophenol and glutamic acid. In both of these there is an amino group for cementing the compound to the mineral, and the molecules thus oriented present water-avid groups (OH and COOH respectively). Dinitrophenol (No. 207) is probably explicable on the same grounds, although the effect is less marked, as is to be expected from the fact that OH is not nearly so vigorous in its capacity to attach organic molecules to sulfides as is $NH_2$, the cementing group in aminophenol. Asparagin, barbituric acid, and uric acid are amides (containing the group $CONH_2$) and this group in a compound is characteristically deterrent to collecting action. (p. 316.) P-nitranilin is interesting when its flotation effect is compared to that with the meta isomer (326) which was tested in the same neutral pulp on the same ore by the same experimenter. The conflicting results indicate that the relative positions of the substituent groups on the benzene ring has a distinct effect on their behavior in flotation, although the data are insufficient to justify setting forth such a conclusion other than tentatively.

The mean number of "insoluble carbons" in this group is 4.8; the percentage having a carbon-oxygen ratio less than 6 is 8.2; the percentage which have a solubility rating of "slight" or less is 31.

Thirteen compounds rate as frothing-depressing agents. The number is too small to permit any generalization on statistical grounds. The compounds are similar in structure to many of those in the O-O and O-D classes. Leucine is an amide; the naphthol orange should be compared with the naphthols (316, 317) to show the effect of the solubilizing $SO_3H$ group. Nos. 30 and 78 are of the general type having polar groups on both ends, which, if they are cemented to the mineral particles render the surface water-avid.

It should be noted that the great majority of substances listed in Table 3 were used with no investigation of their purity and that some of the discrepancies, otherwise unaccountable, may be due to the fact that the substance present was not, actually, the substance named. Many organic chemicals decompose to a greater or less extent standing on the shelf and a majority of the compounds tested were taken from laboratory shelves and used by operators with no knowledge of organic chemistry. It is also to be borne in mind that many of the substances tested react readily with acid or alkali or even with neutral salts, so that it is not safe to conclude (when, *e. g.*, a substance such as methyl red (No. 307) acts so differently in acid and alkaline pulps) that it is the same substance acting in both cases. As a matter of fact this particular substance reacts with alkali to form a different compound and it is to this reaction product that the 46 per cent. collection accredited to methyl red in alkaline pulp is due.

### *Summary of Relation between Chemical Characteristics and Flotation Effect*

The essential characteristics of soluble flotation agents for frothing and collecting may, on the basis of the foregoing tests, be summarized as follows:

1. *Frothing, Noncollecting.*—For this service a reagent should contain an oxygen-bearing, water-avid group, preferably OH, COOH, CO, or COO (COOR) and preferably, also, one such group only. The amide ($CONH_x$) group will serve as the water-avid group, but appears in many instances to have a harmful effect on collecting and should, therefore, be avoided. Attached to the oxygen-bearing group there should be a structure composed of carbon and hydrogen atoms, containing preferably at least six carbon atoms that are not directly attached to the oxygen-bearing group. There must be appreciable solubility but the solubility rating should preferably be "slight;" *i. e.*, around 1000 mg. per l., although many more soluble substances are satisfactory frothers.

2. *Collecting, Nonfrothing.*—These reagents should contain a group of which divalent sulfur or trivalent nitrogen or some other multivalent negative element in the low-valent state is a part. Sulfur in an S-H or S-M (metal) linking is apparently superior to the S-R (hydrocarbon) linkings. The amino ($NH_x$) or diazo (N:N.N) linkings are apparently the best for trivalent nitrogen. The remainder of the molecule should be made of a hydrocarbon complex containing upwards of 8 carbon atoms. If an oxygen-bearing group is present, it is desirable that it be of the C-O-C type. There should be a sensible solubility, but it preferably should not exceed 200 to 300 mg. per l. Ability to form relatively insoluble base-metal salts is probably necessary.

3. *Frothing-collectors.*—These substances must combine the characteristics of the two preceding classes. The best of the class are apparently amines with a hydrocarbon loading upwards of 6. In these the amino group acts both as the water-avid and as the cementing element. There must be sensible solubility and substances whose solubility rates "slight" are probably best. It is possible to change a nonfrothing collector to a frothing-collector by introducing an oxygen-bearing group, but such introduction may defeat the collecting, if the reagent orients on the mineral surface to present the water-avid group outwards, or if the introduction materially increases solubility.

4. *Flotation Inhibitors.*—Reagents that form colloidal solutions almost invariably harm collecting. The sulfonic group ($SO_3H$, $SO_3M$, $SO_3R$) and weakly polar, nonionic halogens are apparently also harmful to collection in most cases. Hence the presence of these groups, either as part of the collecting-agent molecule or introduced in the frother, should be avoided.

## III.—Inorganic Reagents

### *Visible Surface Effects of Flotation Agents*

Tucker and Head[17] pointed out an efficient tool for the investigation of the effects of certain reagents in flotation and themselves applied it to a study of solutions of lime, cyanide and zinc sulfate. They state that 20-min. immersion with agitation, in a solution of zinc sulfate and sodium cyanide (strength not given, but probably from one-half to one part of the cyanide and twice as much zinc sulfate to 8000 parts of water) causes pyrite to lose its luster completely, apparently "due to the quite uniform deposition of salts over the exposed area," accompanied by etching of the surface; that sphalerite is less affected but that there is a distinct deposition of salts, "not nearly so uniform as in the case of pyrite;" while with galena the change in surface is negligible. They give photomicrographs that lend visual support to their statements.

[17] E. L. Tucker and R. E. Head: *Op. cit.*, 354.

Their technique was to cover part of a smooth crystal or cleavage surface of sulfide mineral with paraffin, tie the particle to the impeller shaft of an agitation machine and there expose it for a given time to the reagent solution; remove, wash with distilled water, dry, remove the paraffin and then examine the junction line between the exposed and protected surfaces under reflected illumination with a metallographic microscope.

A protracted experimental campaign was carried out at Columbia in an attempt to verify this work, using at first the methods of Tucker and Head, as learned by correspondence and personal demonstration. Later many variants on their method were devised and tried. As a result of this work it is our belief that none of the reagents used in present-day flotation, except, perhaps, the undissolved part of some oils, and some soluble sulfides, produces, in the usual concentrations, any change in the surface of sulfide minerals that is visible under the microscope, when the reaction investigated is that of a slime-free aqueous solution of the substance on a clean, uncontaminated surface of the sulfide. A number of things were learned in the course of the experimentation that should be of use to other workers.

1. A solution of collodion in ether and alcohol such as the ordinary liquid court-plaster of commerce is much better as a protective coating than paraffin. The latter produces erratic and unpredictable visible surface contamination, greater the higher the temperature of the water used; it changes the surface that has been coated, increasing its tendency to repel water, so that captive-bubble tests thereon are unreliable; it does not cling well in cold water and clean removal is impossible in summer weather. Collodion, on the other hand, does not contaminate the adjacent mineral surface, and in most cases comes off so as to leave no visible residue. It, like paraffin, affects the behavior of the surface that has been coated toward bubbles, making it highly resistant to displacement of water; *i. e.*, to bubble attachment.

2. Crystal faces of some sulfide minerals (*e. g.*, pyrite and galena) are almost invariably coated with a film, probably of some oxidation product (p. 305) which, while it may be insufficient to affect the luster to the naked eye, is strikingly apparent at 100 to 300 magnifications with reflected light. Similar alteration, usually less highly developed, is to be found on many cleavage surfaces even when fresh. If such altered surfaces are used in experiments of the type under discussion, the protective material, paraffin or collodion as the case may be, frequently removes part or all of the altered layer, leaving a fresh and highly reflecting sulfide surface, and thereby giving the erroneous impression, if the assumption is made that the whole surface was originally of this character, that the surface exposed to the solution has been altered. This, according to our experience at Columbia, is the probable explanation of Fig. 16 of the Tucker and Head paper.

3. Freshly cleaved mineral surfaces and, to a far greater extent, crystal surfaces, are frequently heavily covered with dust, either rock dust or extraneous inorganic and organic material. This is not visible to the naked eye or under a low-power microscope but is visible at 100 magnifications with reflected light. It is practically impossible to remove by washing, or by any kind of brushing that does not injure the particle surface. They are, however, quite efficiently removed in peeling off coatings such as those of paraffin or collodion used for protective purposes in these experiments. The result is a clean reflecting surface that contrasts strikingly with the adjacent dusty surface. Some such phenomenon may account for part, although probably not all, of the contrast shown in Fig. 15 of the Tucker and Head paper.

4. The dissolved salts in even extremely dilute solutions leave, on evaporation, deposits which, in the microscopic methods under discussion, show up strikingly. Worse, these deposits are concentrated along the edge of the protective coating, due to the water-shedding character of the protecting materials, so that unless great care is taken in washing, the precipitate from evaporation appears as a coating on the exposed mineral surface. This fact was discovered by noting that the outline of some of the erratically contaminated surfaces observed in our earlier experiments was sharp and curved. Subsequent experiment showed that after removal from solution the particles must, without allowing them to dry, be put through at least three successive washes with distilled water and then dried rapidly before a fan to prevent drop formation as far as possible, and that even under this treatment evaporation contamination must be watched for.

5. Minute quantities of undissolved oil may produce striking surface coatings. The usual sources in experiments of the type under discussion are the atmosphere, the operators' hands and tools, the bearings of the agitation machine, the protective coating, *e. g.*, paraffin, and finally anything of any kind which has not been rendered oil-free that comes into contact with the particle surface. Surfaces that had been determined microscopically clean have shown, after a half-hour's exposure to the laboratory atmosphere, marked evidence of oil contamination. Finger prints constitute the grossest kind of visible contamination (Fig. 7). Lubricating oil or grease from impeller bearings will, unless excluded, cause visible contamination. Silk or cotton thread or wire used to tie particles to the impeller shaft may bring grease to the particle surfaces and this is almost invariably the case if the naked fingers are used for handling.

Our final laboratory procedure, after all of these facts had been determined, involved working throughout with rubber gloves that were kept grease free; handling particles with grease-free tongs, cleaving tools, and the like; examining the particles by reflected light before testing to

insure freedom from oxidation or other surface alteration of a chemical type, and brushing the surface, if necessary, with lens paper on a rubber-covered stirring rod to remove loosely adherent dust; using liquid collodion in a grease-free solvent for a protective coating and cleaned copper wire to tie particles to the impeller shaft; covering the solution container with a tight-fitting cardboard cover to exclude bearing grease; passing the particles after removal from solution through three successive washes of distilled water with no time for drying until after the final wash, then drying in a blast of air from a fan, and examining the particles immediately thereafter before atmospheric or other accidental contamination could occur.

With the procedure just described neither galena, sphalerite nor pyrite shows the slightest sign of surface alteration following 40 min. agitation in solutions of alkaline cyanides, alkaline cyanides plus zinc sulfate, lime, sodium bicarbonate, sodium carbonate, sulfuric acid (if copper is excluded) or any other inorganic reagents tested. The same lack of visible effect is found when the reagents in solution are cresol, potassium xanthate, the soluble part of pine oil, thiocarbanilid or other soluble organic collecting or frothing agents.

### *Slime Coatings*

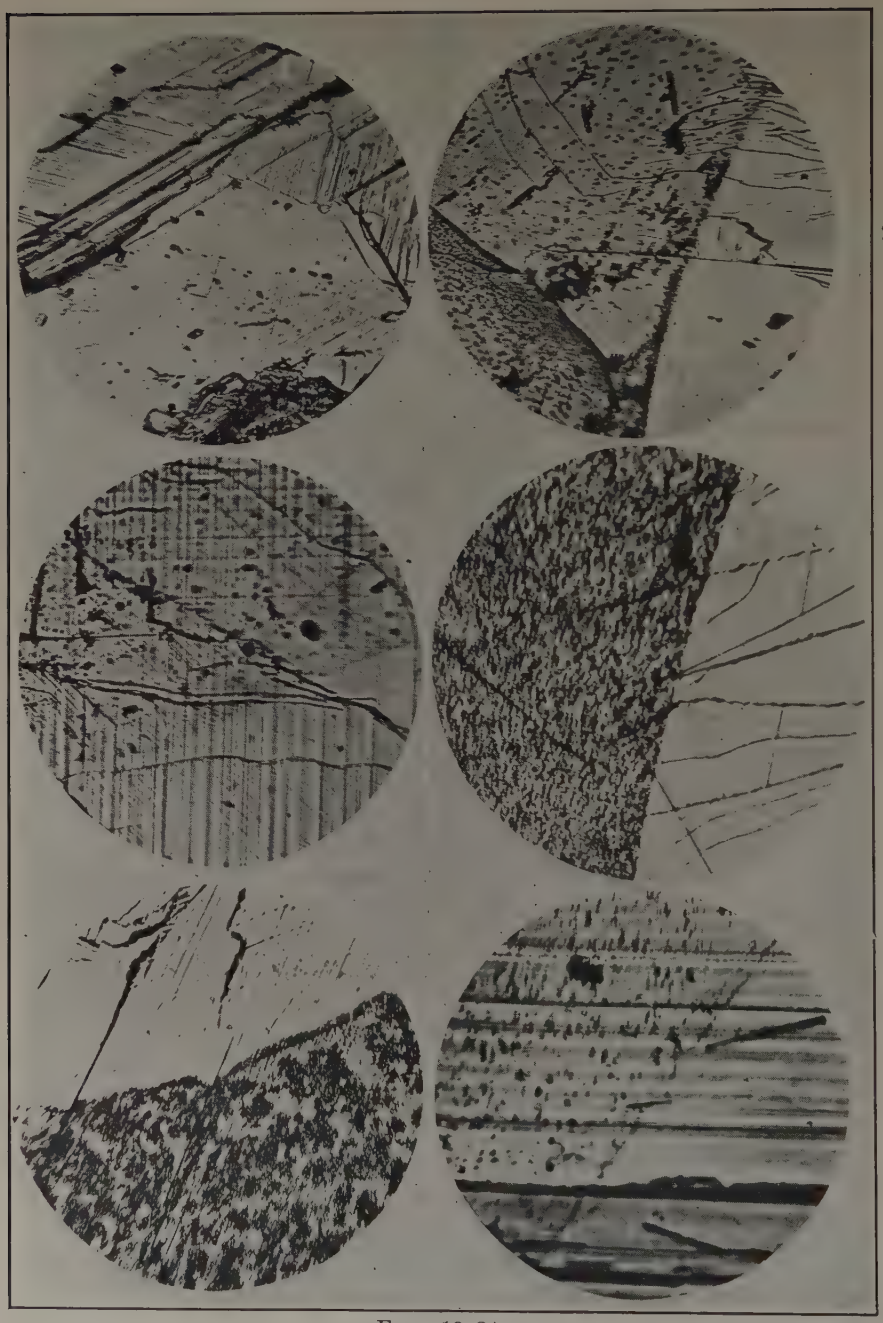
In the course of a series of experiments with chromate alteration of galena surfaces it was found that the presence of minute amounts of albumen in the chromate solution greatly lessened the attack of the chromate. The effect is shown by comparison of Fig. 19, which shows the junction between protected and exposed surfaces on a piece of galena treated for 30 min. at 140° F. in a solution containing 125 mg. pine oil, 250 mg. soda ash, 1000 mg. potassium dichromate and 50 mg. albumen per liter of water, with Fig. 20 in which the albumen is absent; bearing in mind that without either albumen or dichromate present, the surface effect of the mixture of other reagents listed is no greater than that shown in Fig. 19. Albumen forms a colloidal solution and on the theory that it was the adsorption of colloid at the galena surface that prevented the chromate attack, a parallel experiment was tried in which a colloid-like gangue slime (Anaconda) took the place of the albumen in the reagent mixture. The result is shown in Fig. 21.

It is apparent from analysis of the results of these last two experiments that either the colloidal albumen and the pseudocolloidal slime coated the sulfide and prevented the chromate ions from coming into contact therewith, or they themselves reacted with the chromate and consumed it. The former seemed the logical conclusion, in view of the fact that the color of the chromate solution was unchanged by either the albumen or the slime, but it did not seem logical, if slime adsorption was occurring, that

19 20

21 22

23 24



FIGS. 19–24.

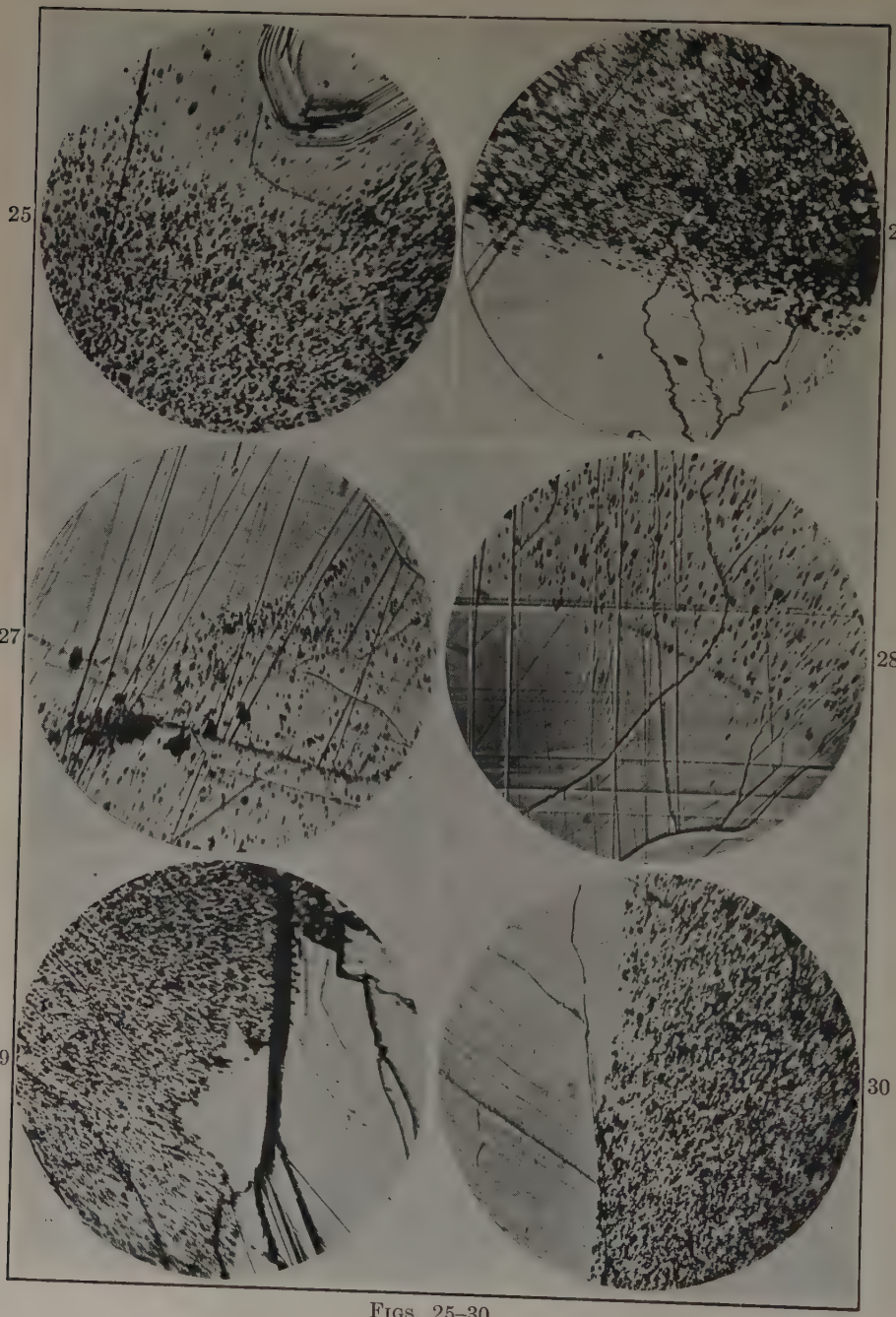
there was not more evidence in the form of slime particles on the exposed surface in Fig. 21. Slime with pine oil (20 mg. per l.) on galena (30 min. exposure at normal temperature) gave a surface coating such as that shown in Fig. 22, which indicates that in addition to the fact that this slime inhibits attack by dichromate on galena, the dichromate or the sodium carbonate, or both together, at the same time do something to the slime that prevents it from coating the galena to the full extent of the possibility indicated in Fig. 22. In Fig. 23 is shown the surface alteration on galena when 125 mg. pine oil, 250 mg. sodium carbonate, 1000 mg. potassium dichromate and 50 mg. of albumen *plus* Anaconda slime act on galena at 140° F. for 30 min. The alteration is of the yellow type characteristic of chromate attack. Clearly the co-presence of the two colloidal materials has nullified the protecting action of both of them. The slime appeared to be dispersed, so that mutual flocculation of the colloidal materials would not appear to be the explanation, although the method of examination of the dispersion with transmitted light under high magnification, since developed, was not applied, so it is not possible to state definitely that the slime was not flocculated.

Our work next took the direction of studying the effect of various electrolytes on the behavior of various slimes toward the surfaces of various sulfide minerals, it having been shown that bubble attachment in solutions of collecting agents was lessened, if not entirely inhibited, by slime coatings on the sulfide particles.

Procedure in all slime tests, unless otherwise noted was as follows:

Clean, unoxidized cleavage surfaces of sulfides on particles about ⅛ to ¼ in. in size were partly coated with collodion and then kept under glass while the slime pulp was made up. The slime pulp was prepared by shaking up 500 g. of solid, ground dry through a 65-mesh screen, with enough distilled water to make a combined volume of 2000 c.c. in a 2000-c.c. graduated cylinder (3 in. dia. by 18 in. deep) allowing the mixture to settle for 2 min. and decanting 1000 c.c.; 500 c.c. of this slime with reagents and with the particles to be tested was then placed in a baffled cylindrical cell, 5 in. dia. by 7 in. deep, and agitated for the required time by means of an impeller, 1 in. from tip to tip of blades, blades and shaft being hollow to cause plentiful aeration of the pulp. After treatment in the pulp the particles were removed, rinsed in tap water, washed through three successive lots of distilled water, dried quickly before a fan and kept under glass for the short time (rarely more than 2 hr.) required for making photomicrographs.

Time is a factor in the amount of coating, as is shown in Figs. 24 to 26, representing 1, 5 and 30 min. exposure respectively of galena to Anaconda slime with no added reagents. The amount of surface contamination was slight in the first minute, but within 5 min. there was strong contamination and 30-min. exposure changed the surface so greatly that for flotation




FIGS. 25–30.

purposes it was substantially gangue rather than sulfide. Sphalerite acted in the same way. This explains a phenomenon familiar to laboratory experimenters, that when using dry-ground feed in laboratory flotation tests, if, for some reason or other a test is interrupted for a considerable time and flotation then attempted, results are frequently not so good as in tests carried through without delay. In terms of this evidence, such is the result when the ore is one in which, during the interruption, heavy gangue coatings form on the sulfides, and subsequent attempts to float have to deal with surfaces in which there is little difference between gangue and sulfide minerals.

Figs. 27 to 29 (galena with Anaconda slime and one part of a mixture of 90 parts Barrett No. 4 coal-tar creosote and 10 parts pine oil to 50,000 of water; 1, 5 and 30 min. exposure respectively) show that the case is similar when oil is present; with this difference, however, that gangue coatings form more slowly with this particular oil combination in the pulp. Thus after 5 min. (Fig. 28) galena is little, if any, more heavily coated than after one minute (Fig. 27). The heavy coating after 30 min. (Fig. 29) suggests an explanation for the bad effects of so-called overagitation in tests where a good initial froth, if not removed, breaks down and cannot be reformed or only on the addition of relatively large amounts of new oil.

One effect of overoiling is shown in Figs. 30 and 31—galena (Fig. 30) and sphalerite (Fig. 31) after 1 min. exposure to the same conditions as in Figs. 28 to 30 except that four times as much oil was present. Both the galena and sphalerite carry heavy gangue coatings after the 1-min. exposure, making them difficult to float and also causing them to carry much gangue into concentrate, if flotation conditions are intensified to the point where they are finally lifted over.

The action of different gangue slimes toward the same sulfides is markedly different, as may be seen by comparing Figs. 32 to 34 (galena, exposed 1, 5 and 30 min. respectively, to a quartz slime pulp, no added reagents), with Figs. 24 to 26. The quartz particles were just as small as the Anaconda slime particles, so far as ordinary microscopic inspection could tell and under certain conditions (Figs. 38 and 39) coated the galena just as heavily. The behavior of sphalerite in the quartz slime was the same as that of galena.

Pine oil and potassium xanthate in the usual flotation quantities (25 mg. per l. and 25 to 60 mg. per l. respectively) make no difference in the behavior of either quartz or Anaconda slimes toward either sphalerite or galena.

The presence of certain soluble inorganic compounds causes amazing differences in the behavior of the gangue slimes. Thus lime in the proportion of 500 mg. per l. (equivalent to about 4 lb. per ton of ore in the usual pulp) substantially prevents deposition of Anaconda slime on

31 32

33 34

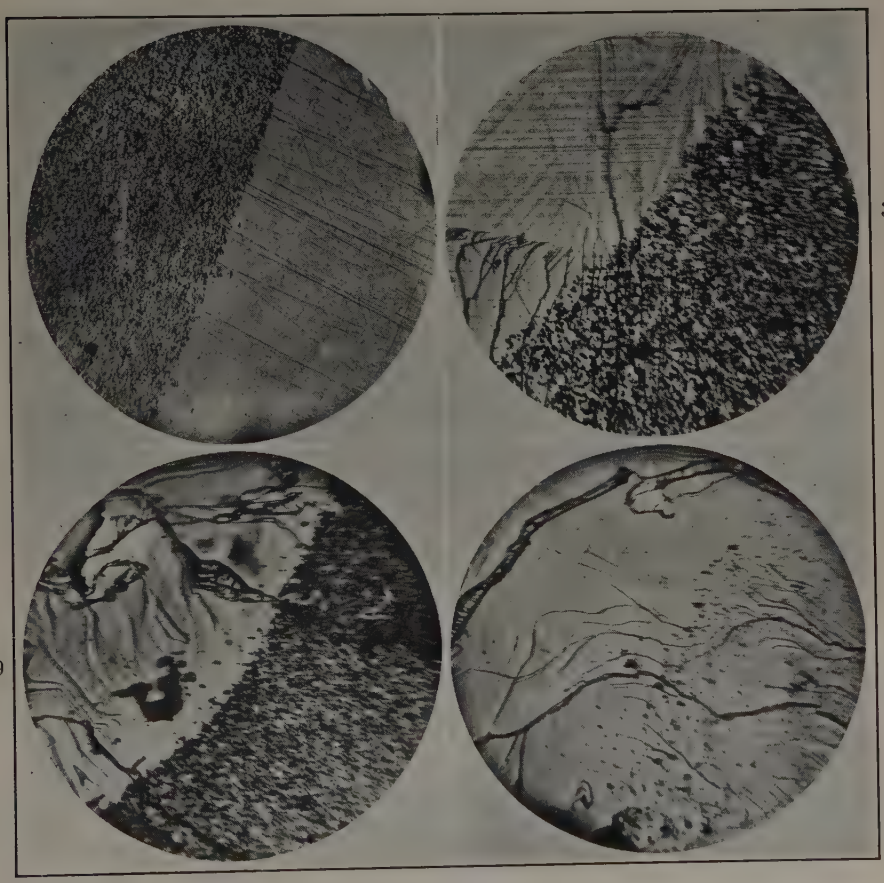
35 36

FIGS. 31–36.

galena (Fig. 35). This figure is directly comparable with Fig. 25, the only difference in conditions being the presence of lime in the pulp of Fig. 35. The same is true with chalcopyrite (Fig. 36, Anaconda slime, 4 lb. lime) although this latter mineral, like galena, is heavily coated in the absence of lime (Fig. 37, Anaconda slime alone). On the other hand, when lime is added to a quartz-slime pulp, deposition on the sulfides is markedly enhanced [compare Figs. 38 (galena, 4 lb. lime, 1 min.)

37 38

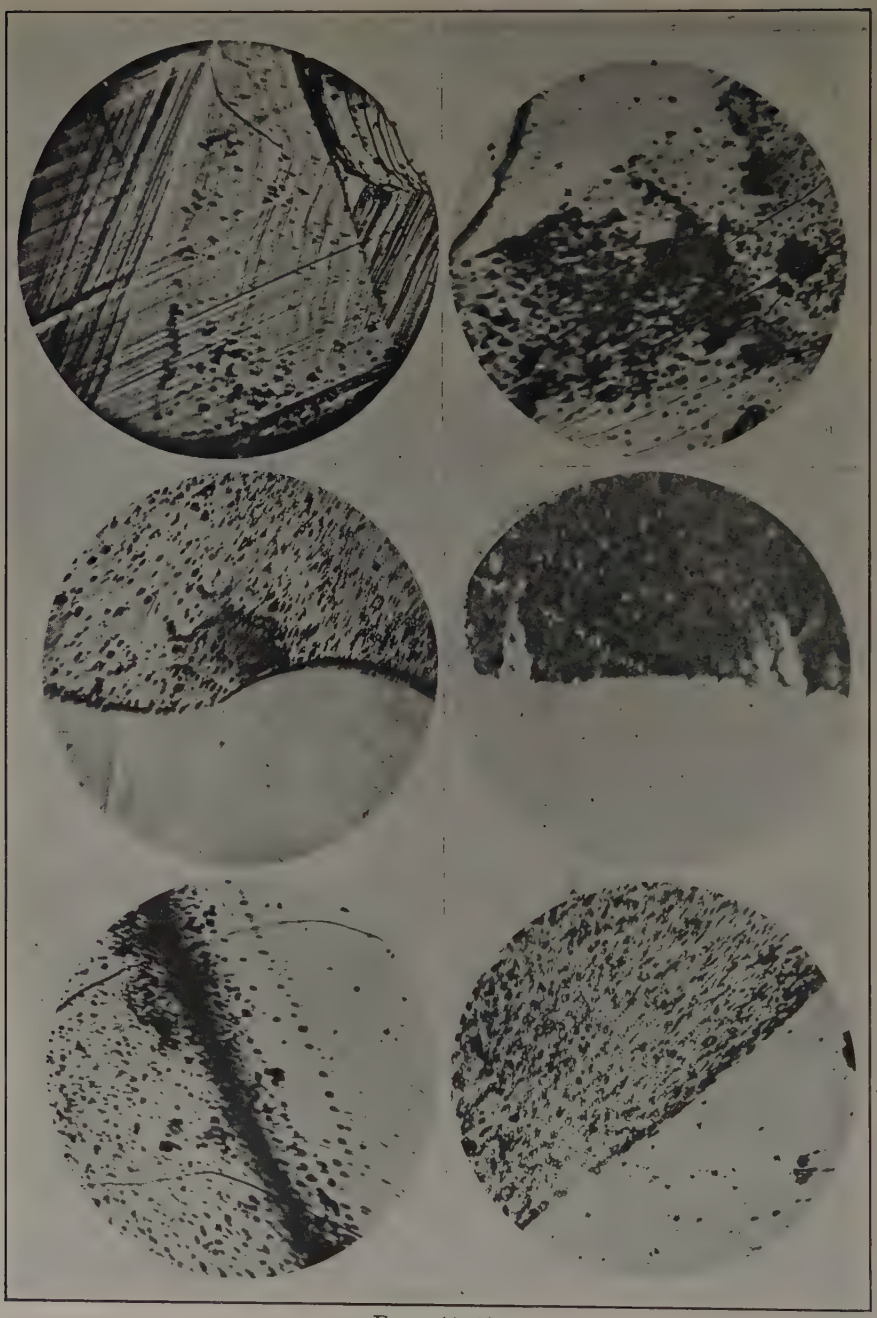
39 40



Figs. 37–40.

and 39 (sphalerite, 4 lb. lime, 1 min.) with Figs. 32 and 40 (sphalerite, no reagent, 1 min.) respectively].

The practical prediction from these coating tests, taken in connection with bubble-machine tests run parallel with them, was that galena and sphalerite could be floated by pine oil and potassium xanthate in a quartz-slime pulp without lime (or any other reagent) and that the addition of lime would injure the flotation; that in Anaconda slime these same miner-




FIGS. 41–46.

als (as well as chalcopyrite and chalcocite, which act similarly), with the same collecting and frothing reagents, would float poorly without lime but well with lime present. Flotation tests confirmed the prediction fully.

While lime is the reagent whose effects have been pictured, additional experiments have proved that it may be taken as typical of the other inorganic reagents that have been used in ordinary collective flotation. Sodium carbonate, sodium bicarbonate, sodium hydroxide, potassium tartrate, sulfuric acid, alum, barium chloride, etc., have been found to have similar effects, differing with the particular sulfide and gangue present.

A possible explanation of a part of the phenomena of differential flotation is to be had from a study of Figs. 41 to 46. Fig. 41 shows galena and Fig. 42 sphalerite after 30 sec. exposure in Anaconda slime pulp containing 330 mg. sodium bicarbonate, 125 mg. potassium cyanide, 250 mg. of zinc sulfate and 33 mg. of coal-tar creosote per liter of water. Addition to the Anaconda-slime pulp of cyanide and zinc sulfate (the bicarbonate was independently proved to be not effective alone) prevented any considerable slime deposition on galena (compare Fig. 41 with Fig. 30) without materially changing that on the sphalerite (compare Fig. 42 with Fig. 31). Pyrite also has a fairly heavy coating (Fig. 43) in the presence of these reagents. Under relatively weak flotation conditions galena might be expected to float away from blende and pyrite in this pulp. Subsequent addition of more oil together with copper sulfate caused little change in the blende coating (Fig. 45) although visual inspection indicates a slight reduction, but it does cause a marked increase in the coatings on galena (Fig. 44) and pyrite (Fig. 46). Hence flotation conditions can be intensified sufficiently to float the blende without effecting any considerable raising of galena and pyrite.

C. R. Ince has done a considerable amount of further work on differential flotation since the work just reported was finished and has found that the differences in slime behavior recorded here do not necessarily account for all of the differences in floatability of the minerals. This work, which is recorded in detail in another paper at this same session,[18] shows that although slime-free solutions of cyanide, zinc sulfate, and copper sulfate produce no visible changes at the surfaces of sulfide minerals, they do, nevertheless, effect marked changes in the floatability of the minerals, as measured by the bubble machine, and that these changes are in the same directions as those indicated by the slime tests and would equally well account for differential flotation. It is probable that the complete successful operation of differential flotation processes with these and similar reagents depends in part on both sets of phenomena.

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[18] See page 261.

TABLE 1.—*Collecting Indices Against Galena for Various Flotation Reagents*

| Reagent | | Water | | Reagent | | Collecting Index, Direct | Relativ Collecting Index |
|---|---|---|---|---|---|---|---|
| Name | Quantity[a] Mg. per L. | Contact Angle, Deg. | Distortion Ratio | Contact Angle, Deg. | Distortion Ratio | | |
| Acetyl diazo amino benzene. ... | 50 | 21 | 0.30 | 41.5 | 0.38 | 14.2 | 40 |
| Amino azo benzene..... | 250 | 28.5 | 0.32 | 37.5 | 0.35 | 6 | 17 |
| Amyl disulfide..... | 50 | 12 | 0.16 | 47 | 0.46 | 31.5 | 89 |
| Amyl mercaptan..... | 50 | 19 | 0.25 | 33 | 0.44 | 16.5 | 46 |
| Amyl xanthate..... | 25 | 16 | 0.17 | 60 | 0.40 | 33.5 | 94 |
| Azo benzene..... | 250 | 29 | 0.32 | 53.5 | 0.49 | 20.8 | 59 |
| Azo naphthalene [α, α]..... | 40 | 10.5 | 0.08 | 43 | 0.40 | 31 | 87 |
| Benzamide..... | 40 | 12 | 0.11 | 12 | 0.15 | 2 | 6 |
| Benzene azo diphenyl urea..... | 50 | 15 | 0.18 | 28 | 0.41 | 18 | 51 |
| Benzene azo [α] naphthol..... | 40 | 10 | 0.11 | 14 | 0.23 | 8 | 23 |
| Benzene azo [α] naphthol..... | 1250 | 11 | 0.09 | 36 | 0.32 | 24 | 68 |
| Benzene diazo amino [p] toluene. | 40 | 9.5 | 0.08 | 14.5 | 0.18 | 7.5 | 21 |
| Benzene diazo amino [p] toluene. | 1250 | 12.5 | 0.06 | 40.5 | 0.34 | 28 | 79 |
| Benzidine..... | 50 | 16 | 0.24 | 16 | 0.28 | 2 | 6 |
| Benzyl amine..... | 50 | 16.5 | 0.14 | 20.5 | 0.25 | 7.5 | 21 |
| Benzyl diazo amino benzene.... | 50 | 18 | 0.21 | 37 | 0.37 | 9.5 | 27 |
| Butyl sulfone [n]..... | 40 | 11.5 | 0.10 | 15.5 | 0.21 | 7.5 | 21 |
| Carbothialdin..... | 250 | 24 | 0.23 | 42 | 0.43 | 19 | 54 |
| Carbothialdin..... | 375 | 16 | 0.17 | 36.5 | 0.31 | 17.2 | 48 |
| Carvacrol..... | 50 | 18 | 0.24 | 22 | 0.27 | 3.5 | 10 |
| Carvacrylamine..... | 50 | 25 | 0.28 | 35 | 0.34 | 8 | 23 |
| Chlor nitrobenzene..... | 250 | 33.5 | 0.38 | 36.5 | 0.39 | 2 | 6 |
| Chrysoidin..... | 50 | 12 | 0.10 | 40 | 0.30 | 24 | 68 |
| Cresol..... | 25 | 16 | 0.21 | 17 | 0.23 | 1.5 | 4 |
| Cresol..... | 125 | 15 | 0.16 | 19 | 0.26 | 7 | 21 |
| Dehydro thio [p] toluidin..... | 40 | 12.5 | 0.08 | 27 | 0.33 | 19.8 | 56 |
| Diazo amino benzene..... | 100 | 14 | 0.16 | 40 | 0.39 | 24.5 | 69 |
| Diazo benzene imid..... | 50 | 19 | 0.26 | 42 | 0.42 | 19.5 | 55 |
| Dichlor benzene..... | 250 | 34 | 0.37 | 34 | 0.37 | 0 | 0 |
| Diphenyl thio carbamate..... | 250 | 28 | 0.25 | 41 | 0.38 | 13 | 36 |
| Diphenyl thio carbazid..... | 50 | 14.5 | 0.22 | 37 | 0.34 | 17.5 | 49 |
| Ditolyl thio urea..... | 25 | 27 | 0.32 | 48 | 0.41 | 15 | 42 |
| Dixanthogen..... | 25 | 19 | 0.20 | 44.5 | 0.34 | 19.8 | 56 |
| Dixanthogen..... | 40 | 13 | 0.19 | 41 | 0.38 | 23.5 | 66 |
| Ethyl ethyl xanthate..... | 250 | 27 | 0.23 | 37.5 | 0.30 | 8.2 | 23 |
| Ethyl methyl xanthate..... | 250 | 22 | 0.21 | 50 | 0.37 | 22 | 62 |

[a] The quantity in this column was added per liter of water, stirred in a 4-in. square glass jar with a 3-in. cross-armed agitator for 10 min. at 1000 to 1500 r. p. m., then filtered through infusorial earth.

TABLE 1.—(*Continued*)

| Reagent | | Water | | Reagent | | Collecting Index, Direct | Relative Collecting Index |
|---|---|---|---|---|---|---|---|
| Name | Quantity[a] Mg. per L. | Contact Angle, Deg. | Distortion Ratio | Contact Angle, Deg. | Distortion Ratio | | |
| Ethyl xanthogen ethyl formate.. | 25 | 17 | 0.19 | 47 | 0.34 | 22.5 | 63 |
| Heptyl mercaptan | 50 | 18 | 0.22 | 27.5 | 0.35 | 11 | 31 |
| Heptyl sulfide | 50 | 15 | 0.15 | 17 | 0.23 | 5 | 14 |
| Hydroquinone | 25 | 33.5 | 0.34 | 33 | 0.31 | −1.8 | −5 |
| Hydroquinone | 125 | 32.5 | 0.33 | 34 | 0.33 | 1.5 | 4 |
| Hydroxy azo benzene | 250 | 25 | 0.29 | 31 | 0.29 | 3 | 8 |
| Lead xanthate | 2.5 | 13 | 0.07 | 46.5 | 0.40 | 34.8 | 98 |
| Mercapto benzo thiazole | 25 | 13 | 0.13 | 17.5 | 0.29 | 10.2 | 29 |
| Naphthol [β] | 50 | 16 | 0.17 | 23.5 | 0.29 | 9.8 | 28 |
| Naphthylamine [α] | 25 | 15.5 | 0.15 | 40 | 0.35 | 22 | 62 |
| Naphthylamine [α] | 125 | 19 | 0.27 | 46 | 0.41 | 20.5 | 58 |
| Naphthylamine [β] | 50 | 13 | 0.07 | 35.5 | 0.27 | 21.5 | 61 |
| Nitrobenzol | 250 | 29 | 0.30 | 31 | 0.34 | 3 | 8 |
| Oil | | | | | | | |
| Barrett No. 4, coal-tar creosote | 25[b] | 18 | 0.08 | 18 | 0.09 | 0.5 | 1 |
| Blast-furnace creosote | 25[b] | 17 | 0.15 | 20 | 0.16 | 2 | 6 |
| Fuel oil (asphaltum-base residuum) | 25[b] | 17 | 0.22 | 16 | 0.20 | −0.5 | −1 |
| Kerosene acid sludge | 25 | 13.5 | 0.14 | 14.5 | 0.16 | 1.5 | 4 |
| Kerosene acid sludge | 250 | 32.5 | 0.36 | 37.5 | 0.39 | 4 | 11 |
| Nujol | 25[b] | 15 | 0.14 | 35 | 0.18 | 12 | 34 |
| Pine oil | 20[b] | 29 | 0.24 | 29 | 0.25 | 0 | 0 |
| Pine oil | 20 | 29 | 0.29 | 30 | 0.35 | 3.5 | 10 |
| Turpentine | 250 | 19 | 0.20 | 18 | 0.29 | 4 | 11 |
| Wood creosote | 25[b] | 15 | 0.13 | 24 | 0.24 | 10 | 28 |
| Phenyl hydrazine | 50 | 14.5 | 0.12 | 35.5 | 0.33 | 21 | 59 |
| Phenyl iso thiocyanate | 40 | 11 | 0.10 | 30 | 0.31 | 20 | 56 |
| Phenyl salicylate | 125 | 22 | 0.29 | 24 | 0.33 | 3 | 8 |
| Phenyl thio urea | 25 | 17.5 | 0.23 | 43 | 0.40 | 21.2 | 59 |
| Phenyl thio urethane | 25 | 16.5 | 0.17 | 35.5 | 0.44 | 23 | 65 |
| Phenyl urea | 125 | 28 | 0.30 | 26 | 0.28 | −2 | −6 |
| Potassium salicylate | 125 | 28.5 | 0.33 | 33.5 | 0.33 | 2.5 | 7 |
| Potassium xanthate | 25 | 14.5 | 0.10 | 54 | 0.42 | 35.5 | 100 |
| Salicylic acid | 125 | 22 | 0.25 | 26 | 0.28 | 3.5 | 10 |
| Seleno benzamide | 40 | 12 | 0.08 | 35 | 0.43 | 29 | 82 |

[b] Unfiltered emulsion.

TABLE 1.—(*Continued*)

| Reagent | | Water | | Reagent | | Collecting Index, Direct | Relative Collecting Index |
|---|---|---|---|---|---|---|---|
| Name | Quantity[a] Mg. per L. | Contact Angle, Deg. | Distortion Ratio | Contact Angle, Deg. | Distortion Ratio | | |
| Sodium di thio phenyl carbamate | 40 | 17.5 | 0.19 | 51.5 | 0.42 | 28.5 | 80 |
| Tetraethyl ammonium hydroxide | 50 | 19.5 | 0.26 | 15.5 | 0.22 | −4 | −11 |
| Tetramethyl ammonium hydroxide | 50 | 22 | 0.21 | 19.5 | 0.18 | −3.8 | −11 |
| Tetrapropyl ammonium hydroxide | 50 | 13.5 | 0.15 | 17 | 0.19 | 3.8 | 11 |
| Thialdin | 50 | 15 | 0.13 | 32 | 0.28 | 16 | 45 |
| Thialdin | 250 | 12.5 | 0.12 | 42 | 0.37 | 27.2 | 77 |
| Thioanilin | 50 | 24 | 0.28 | 42 | 0.40 | 15 | 42 |
| Thiocarbanilid | 50 | 12 | 0.12 | 54 | 0.41 | 35.5 | 100 |
| Thiocresol | 40 | 12 | 0.08 | 67 | 0.46 | 46.5 | 131 |
| Thiophenol | 50 | 17 | 0.19 | 50 | 0.47 | 30.5 | 86 |
| Thiourea | 125 | 27.5 | 0.35 | 32 | 0.34 | 1.8 | 5 |
| Toluene azo resorcinol [p] | 40 | 10.5 | 0.07 | 34 | 0.34 | 25.2 | 71 |
| Toluidin [o] | 100 | 25.5 | 0.27 | 38 | 0.29 | 7.2 | 20 |
| Trichlor benzene | 250 | 24 | 0.23 | 26 | 0.22 | 0.5 | 1 |
| Urea | 125 | 26.5 | 0.34 | 33 | 0.39 | 5.8 | 16 |
| Xanthic acid | 250 | 17 | 0.23 | 52.5 | 0.44 | 29.2 | 82 |
| Xanthic anhydride | 25 | 12 | 0.06 | 58.5 | 0.48 | 44.2 | 124 |
| Xanthogenamide | 25 | 12.5 | 0.08 | 40 | 0.39 | 29.2 | 82 |
| Xylenol | 50 | 11 | 0.11 | 16 | 0.20 | 7 | 19 |
| Xylidin | 50 | 16 | 0.16 | 18 | 0.19 | 2.5 | 7 |

TABLE 2.—*Results of Frothing Tests in Apparatus of Fig.* 13

| Test No. | Reagent | Concentration Mg. per L. | Per Cent. Solids in Froth | Solids in Overflow, G. per Cu. Ft. Air | Water in Overflow, G. per Cu. Ft. Air | Total Overflow, G. per Cu. Ft. Air | Total Overflow, G. per Cu. Ft. Air per Mg. of Reagent per Liter Water |
|---|---|---|---|---|---|---|---|
| 68 | Distilled water | 1,000,000 | 20.4 | 3.3 | 12.8 | 16.1 | ∞ |
| 130–3 | Pine oil | 10 | 19.1 | 5.6 | 23.7 | 29.3 | 2.9 |
| 128, 129 | Pine oil | 20 | 16.5 | 6.4 | 32.1 | 38.5 | 1.9 |
| 126, 127 | Pine oil | 40 | 16.1 | 7.6 | 39.6 | 47.2 | 1.2 |
| 123–5 | Pine oil | 60 | 15.1 | 8.5 | 47.4 | 55.9 | 0.93 |
| 118, 120–2 | Pine oil | 80 | 14.9 | 9.0 | 51.6 | 60.6 | 0.76 |
| 134–6 | Pine oil | 100 | 14.1 | 9.1 | 55.5 | 64.6 | 0.65 |
| 138, 139 | Pine oil | 120 | 13.2 | 8.8 | 58.8 | 67.6 | 0.56 |
| 141, 142 | Pine oil | 140 | 14.7 | 10.6 | 61.3 | 71.9 | 0.51 |
| 143, 144 | Pine oil | 320 | 15.4 | 11.2 | 62.1 | 73.3 | 0.23 |
| 145–7 | Pine oil solution[a] | 20 | 18.6 | 7.1 | 30.5 | 37.6 | |
| 55, 58 | Terpineol | 25 | 20.1 | 10.0 | 39.6 | 49.6 | |
| 95, 96 | Phenol | 125 | 19.6 | 3.4 | 14.1 | 17.5 | 1.4 |
| 93, 94 | Phenol | 25 | 20.0 | 4.8 | 19.3 | 24.1 | 1.0 |
| 91, 92 | Phenol | 50 | 19.3 | 4.8 | 20.3 | 25.1 | 0.50 |
| 89, 90 | Phenol | 75 | 21.7 | 6.2 | 22.4 | 28.6 | 0.39 |
| 87, 88 | Phenol | 100 | 22.4 | 6.9 | 24.0 | 30.9 | 0.31 |
| 84, 86 | Phenol | 150 | 22.2 | 7.7 | 26.6 | 34.3 | 0.23 |
| 79, 81, 82 | Phenol | 200 | 23.8 | 8.2 | 25.5 | 33.7 | 0.18 |
| 148, 149 | Cresol | 20 | 17.0 | 5.8 | 28.4 | 34.2 | 1.7 |
| 150, 151 | Cresol | 40 | 16.3 | 7.0 | 36.4 | 43.4 | 1.1 |
| 152, 153 | Cresol | 60 | 15.3 | 7.5 | 36.6 | 44.1 | 0.74 |
| 154, 155 | Cresol | 80 | 15.2 | 7.0 | 39.5 | 46.5 | 0.58 |
| 156, 157 | Cresol | 100 | 16.2 | 8.4 | 43.8 | 52.2 | 0.52 |
| 158, 159 | Cresol | 140 | 15.2 | 8.0 | 44.9 | 52.9 | 0.38 |
| 160, 161 | Cresol | 160 | 15.1 | 8.6 | 56.6 | 65.2 | 0.41 |
| 162, 163 | Cresol | 200 | 14.1 | 9.1 | 55.8 | 64.9 | 0.32 |
| 97, 99 | Aniline | 200 | 17.3 | 4.7 | 22.6 | 27.3 | |
| 100, 101 | Aniline | 400 | 18.4 | 6.6 | 36.0 | 42.6 | |
| 40, 42–44 | Toluidin | 25 | 18.6 | 4.3 | 18.7 | 23.[illegible] | |
| 102, 103 | Toluidin | 200 | 17.8 | 6.8 | 31.2 | 38.0 | |
| 104, 105 | Toluidin | 400 | 15.8 | 7.8 | 41.2 | 49.0 | |
| 47, 48 | Xylidin | 25 | 18.0 | 5.2 | 23.4 | 28.6 | |

[a] Filtrate from an emulsion of the stated concentration.

TABLE 3.—*Flotation Effect of Various Organic Chemical Compounds*

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[e] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Froth-ing | Collect-ing | Froth-ing | Collect-ing | Froth-ing | Collect-ing | | | |
| 1 | Abietic acid | $C_{20}H_{30}O_2$[h] | i | o | o M | o | 51 M | sl | 49 M | F-C | COOH | [h] |
| 2 | Acenaphthene | $C_{10}H_6(CH_2)_2$ | i | | | sl | sl P | | | O-O | None | 12 |
| 3 | Acetal | $CH_3.CH(OC_2H_5)_2$ | 55,000 | | | f | o P | | | F-O | COC | 4 |
| 4 | Acetaldehyde | $CH_3.CHO$ | ∞ | f | 14 M | f | o M | f | o M | F-O | CO | 1 |
| 5 | Acetamide | $CH_3.CO.NH_2$ | v sol | o | o M | o | 10 M | o | 24 M | O-O | $CONH_2$ | 1 |
| 6 | Acetanilid | $C_6H_5.NH.COCH_3$ | 5,000 | g | o M | g | 33 J | g | o M | F-O | CONH | 6 |
| 7 | Acetic acid | $CH_3.COOH$ | ∞ | f | o M | o | o M | o | o M | O-O | COOH | 1 |
| 8 | Acetic anhydride | $(CH_3.CO)_2O$ | d | g | o M | | | o | o M | F-O | CO | 2 |
| 9 | Acetnaphthalid [α] | $C_{10}H_7.NH.COCH_3$ | sl | | | v sl | v sl P | | | O-O | CONH | 10 |
| 9a | Acetnaphthalid [β] | $C_{10}H_7.NH.COCH_3$ | sl | | | f | v sl P | | | F-O | CONH | 10 |
| 10 | Aceto-nitrile | $CH_3.C{:}N$ | ∞ | | | o | o P | | | O-O | C:N | 1 |
| 11 | Acetone | $CH_3.CO.CH_3$ | ∞ | o | o M | | | o | 4 M | O-O | CO | 2 |
| 12 | Acetone phenyl hydrazone | $(CH_3)_2.C{:}N.NH.C_6H_5$ | sl | | | f | f P | | | F-C | N.NH | 7 |
| 13 | Acetone sodium bisulfite | $(CH_3)_2.C(OH)O.SO_3.Na$ | sl | o | o M | | | o | −20 M | O-D | $SO_3M$, OH | 2 |
| 14 | Acetophenone | $CH_3.CO.C_6H_5$ | i | | | g | o P | | | F-O | CO | 7 |
| 15 | Acetoxime | $(CH_3)_2.C{:}N.OH$ | v sol | g | o M | | | g | o M | F-O | OH | 2 |
| 16 | Acetphenetidine | $CH_3.CO.NH.C_6H_4OC_2H_5$ | 1,100 | g | sl M | g | 37 J | g | sl M | F-O | CONH, COC | 7 |
| 17 | Acet-toluide [o] | $CH_3.C_6H_4.NH.COCH_3$ | 8,600 | | | f | v sl P | | | F-O | CONH | 7 |
| 18 | Acetyl diazo amino benzene | $C_6H_5.N{:}N.N(COCH_3).C_6H_5$ | i | | | | | o | 50 C | O-C | N:N, CON''' | 11 |
| 19 | Acetyl phenyl hydrazine | $C_6H_5.NH.NH.COCH_3$ | sl | | | f | sl P | | | F-O | CONH, NH | 6 |
| 20 | Acetyl phenylene diamine | $NH_2.C_6H_4.NH.COCH_3$ | sl | | | v sl | sl P | | | O-O | CONH, $NH_2$ | 5 |
| 21 | Acetyl salicylic acid | $CH_3.CO.O.C_6H_4.COOH$ | sl | g | o M | | | o | o M | F-O | COO, COOH | 5 |
| 22 | Acetyl [o] toluidin | $CH_3.CO.NH.C_6H_4.CH_3$ | 8,600 | | | f | 32 J | | | F-O | CONH | 7 |
| 23 | Acetyl [p] toluidin | $CH_3.CO.NH.C_6H_4.CH_3$ | 900 | | | f | 26 J | | | F-O | CONH | 7 |
| 24 | Acetyl urea | $CH_3.CO.NH.CO.NH_2$ | sol | | | o | 11 J | | | O-O | CONH | 1 |
| 25 | Acridine | [illegible] | v sl | | | v sl | v slP | | | O-O | NH | 11 |
| 26 | Albumen | Unknown; a protein | c | | | o | −72 J | | | O-D | | |
| 27 | Aldehyde ammonia | $CH_3.CH(OH)NH_2$ | v sol | | | v sl | v sl P | | | O-O | $NH_2$, OH | 1 |
| 28 | Aldehyde benzoic acid | $COOH.C_6H_4.CHO$ | v sol | | | g | o P | | | F-O | COOH, CO | 6 |
| 29 | Aldol | $CH_3.CH(OH)CH_2.CHO$ | ∞ | | | g | o C | | | F-O | OH, CO | 2 |
| 30 | Alizarin | $C_6H_4(CO)_2C_6H_2(OH)_2$ | i | f | o M | o | −70 J | o | −24 M | F-D | CO, OH | 10 |
| 31 | Alkamine hydrochloride | $OH.CH_2.CH_2.N(CH_3)_2$ HCl | sol | | | ex | sl J | | | F-O | OH, N''' | 2 |
| 32 | Allyl alcohol | $CH_2{:}CH.CH_2.OH$ | ∞ | f | o M | | | f | o M | F-O | OH | 2 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 33 | Allyl isothio cyanate | $C_3H_5.N:C:S$ | | | | vsl | v sl P | | | O-O | N:C:S | 2 |
| 34 | Amidol | $HO.C_6H_3(NH_2)_2.HCl$ | sol | | | o | 14 J | | | O-O | $[RNH_3]^+$, OH, $[Cl]^-$ | 3 |
| 35 | Amino acetophenone [p] | $NH_2.C_6H_4.COCH_3$ | v sl | f | o M | | | g | sl M | F-O | $NH_2$, CO | 6 |
| 36 | Amino azo benzene | $NH_2.C_6H_4.N:N.C_6H_5$ | v sl | o | o M | o | 69 J | o | 88 M | O-C | N:N, $NH_2$ | 9 |
| 37 | Amino azo benzene hydrochloride. | $NH_2.C_6H_4.N:N.C_6H_5.HCl$ | sol | o | o M | | | sl | 66 M | O-C | N:N, $[RNH_3]^+$, $[Cl]^-$ | 9 |
| 38 | Amino azo naphthalene | $C_{10}H_7.N:N.C_{10}H_6.NH_2$ | i | | | o | f P | o | o C | O-C | N:N, $NH_2$ | 17 |
| 39 | Amino benzoic acid [o] | $NH_2.C_6H_4.COOH$ | [h]3,500 | f | o M | f | v sl P | o | o M | F-O | $NH_2$, COOH | 5 |
| 40 | Amino isobutyric acid | $(CH_3)_2CH_2.CH(NH_2)$-COOH | ∞ | o | −12 M | | | o | v sl M | O-O | $NH_2$, COOH | 3 |
| 41 | Amino phenol [p] | $NH_2.C_6H_4.OH$ | 11,000 | o | −25 M | v sl | v sl P | o | −54 M | O-D | $NH_2$, OH | 4 |
| 42 | Amino phenol hydrochloride [p]. | $NH_2.C_6H_4.OH.HCl$ | sol | | | sl | 44 J | | | O-C | $[RNH_3]^+$, OH, $[Cl]^-$ | 4 |
| 43 | Amino thiophenol | $NH_2.C_6H_4.SH$ | sl | | | v sl | f P | | | O-C | $NH_2$, SH | 4 |
| 44 | Ammonium benzoate | $C_6H_5.COO.NH_4$ | 196,000 | | | o | o J | | | O-O | $[COO]^-$, $[NH_4]^+$ | 6 |
| 45 | Ammonium eosine | [g] | sol | o | −30 M | sl | −23 J | sl | v sl M | O-D | CO, OH, Br, $[NH_4]^+$ | 12 |
| 46 | Ammonium formate | $NH_4.CHO_2$ | 1,020,000 | | | o | o J | | | O-O | CO, $[NH_4]^+$ | 0 |
| 47 | Ammonium phenyl dithiocarbamate. | $C_6H_5.NH.CS.S.NH_4$ | sol | | | o | 70 C | | | O-C | SR, CSNH, $[NH_4]^+$ | 5 |
| 48 | Ammonium succinate | $COOH.CH_2.CH_2.COO.NH_4$ | v sol | f | o M | | | o | v sl M | F-O | COOH, $[NH_4]^+$, COO | 2 |
| 49 | Amygdalic acid | [bj] | sol | | | o | 25 J | | | O-O | COOH, OH, COC | 6 |
| 50 | Amygdalin | [bi] | 83,000 | o | −20 M | sl | 10 J | o | −32 M | O-D | CN, OH, COC | 6 |
| 51 | Amyl acetate | $CH_3.COO.C_5H_{11}$ | 1,800 | g | g C | g | 47 J | ex | 20 C | F-C | COO | 5 |
| 52 | Amyl alcohol | $CH_3.(CH_2)_3.CH_2.OH$ | 27,000 | | | g | sl P | | | F-O | OH | 4 |
| 53 | Amyl bromide (tert.) | $(CH_3)_2.C_2H_5.C.Br$ | i | | | o | o P | | | O-O | Br | 3 |
| 54 | Amyl disulfide | $C_5H_{11}.S.S.C_5H_{11}$ | i | | | | | o | 33 C | O-C | S'' | 8 |
| 55 | Amyl iodide | $CH_3(CH_2)_4I$ | i | | | o | o P | | | O-O | I | 4 |
| 56 | Amyl mercaptan | $C_5H_{11}.SH$ | i | | | | | o | 50 C | O-C | SH | 4 |
| 57 | Amyl nitrate | $C_5H_{11}.NO_3$ | sl | | | g | 46 J | | | F-C | $NO_3$ | 4 |
| 58 | Amyl nitrite | $C_5H_{11}.NO_2$ | sl | | | g | 51 J | | | F-C | $NO_2$ | 4 |
| 59 | Amylene | $CH_3(CH_2)_2CH:CH_2$ | i | | | f | sl P | | | F-O | None (i) | 5 |
| 60 | Aniline | $C_6H_5.NH_2$ | 31,000 | | | f | 62 C | | | F-C | $NH_2$ | 5 |
| 61 | Aniline black | $C_{66}H_{44}NCl_3$[h] | i | sl | o M | | | f | 8 M | F-O | N, Cl | |
| 62 | Aniline blue | $C_{20}H_{16}(C_6H_5)_3N_3.HCl$[h] | sl | o | −63 M | | | o | 15 M | O-D | N''', $[Cl]^-$ | |
| 63 | Aniline green | $C_{22}H_{27}N_3S_2O$[h] | i | o | −95 M | | | o | −63 M | O-D | N''', $S_2O$ | |
| 64 | Aniline hydrochloride | $C_6H_5.NH_2.HCl$ | 31,000 | o | o M | f | 50 M | f | 8 M | F-C | $NH_2$, $[Cl]^-$ | 5 |
| 65 | Aniline nitrate | $C_6H_5.NH_2.HNO_3$ | v sol | o | −18 M | | | sl | sl M | O-O | $NH_2$, $[NO_3]^-$ | 5 |
| 66 | Aniline orange | $CH_3.C_6H_2.(NO_2)_2OK$ | | o | −12 M | sl | 18 J | o | −30 M | O-O | $NO_2$, $[K]^+$ | 4 |
| 67 | Aniline oxalate | $C_6H_5NH_2.(COOH)_2$ | sl | | | f | 67 J | | | F-C | $NH_2$, COOH | 5 |
| 68 | Aniline purple | [j] | i | o | −50 M | | | o | 37 M | O-C | $NH_2$, N''', $[Cl]^-$ | 23 |
| 69 | Aniline red (see Magenta, No. 286) | | | | | | | | | | | |
| 70 | Aniline sulfate | $C_6H_5.NH_2.H_2SO_4$ | 66,000 | o | o M | f | 73 C | o | 16 M | F-C | $NH_2$, $[SO_4]^-$ | 5 |
| 71 | Aniline violet (see Aniline purple, No. 68) | | | | | | | | | | | |
| 72 | Aniline yellow | $C_{10}H_5(NO_2)_2.OK$ (or $ONH_4$) | sol | o | o M | o | 58 J | o | −76 M | O-D | $NO_2$, $[K]^-$ | 7 |
| 73 | Anisol | $C_6H_5.O.CH_3$ | i | | | sl | v sl P | | | O-O | COC | 6 |
| 74 | Anthracene | $C_6H_4(CH)_2C_6H_4$ | i | o | o M | v sl | v sl P | o | o M | O-O | None | 14 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[e] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Frothing | Collecting | Frothing | Collecting | Frothing | Collecting | | | |
| 75 | Anthraquinone | $C_6H_4(CO)_2C_6H_4$ | i | o | o M | o | o J | o | o M | O-O | CO | 12 |
| 76 | Antipyrene | [k] | 1,000,000 | g | −13 M | | | o | o M | O-O | N‴, CON‴ | 9 |
| 77 | Asparagin | $CH_3.C.NH_2(COOH).CO.NH_2$ | 18,000 | | | o | −44 J | | | O-D | COOH, $CONH_2$, $NH_2$ | 1 |
| 78 | Aurin tricarboxylic acid | $COOH(O)C_6H_3:C[C_6H_3(OH)COOH]_2$ | sol | f | −66 M | | | o | o M | F-D | COOH, OH | 16 |
| 79 | Azo benzene | $C_6H_5.N:N.C_6H_5$ | i | o | o M | o | 21 J | o | o M | O-O | N:N | 10 |
| 80 | Azo naphthalene | $C_{10}H_7.N:N.C_{10}H_7$ | i | | | o | sl P | o | o C | O-O | N:N | 18 |
| 81 | Azoxy benzene | $(C_6H_5)_2.N_2O$ | i | o | o M | o | sl P | o | 12 M | O-O | $N_2O$ | 10 |
| 82 | Barbituric acid | $CO:(NH.CO)_2:CH_2 + 2H_2O$ | sl | o | −50 M | o | −21 M | o | −30 M | O-D | CONH | 1 |
| 83 | Benzal acetone | $C_6H_5.CH:CH.COCH_3$ | i | f | o M | f | o M | f | o M | F-O | CO | 9 |
| 84 | Benzal acetophenone | $C_6H_5.CH_2.CO.C_6H_5$ | i | o | 35 M | o | o M | o | o M | O-O | CO | 13 |
| 85 | 5-Benzal amino 2-cresol | $C_6H_5.CH:N.C_6H_3(OH)CH_3$ | sl | o | o M | o | 24 M | f | 65 M | F-C | OH, N‴ | 12 |
| 85a | p-Benzal amino phenol | $OH.C_6H_4.N:CH.C_6H_5$ | sl | f | −32 M | o | 21 M | f | o M | F-O | OH, N‴ | 11 |
| 86 | Benzal azine | $C_6H_5.CH:N.N:CH.C_6H_5$ | i | | | | | o | v sl C | O-O | N‴-N‴ | 12 |
| 87 | Benzaldehyde | $C_6H_5.CHO$ | 3,300 | | | f | o P | | | F-O | CO | 6 |
| 88 | Benzaldehyde phenyl hydrazone | $C_6H_5.CH:N.NH.C_6H_5$ | v sl | | | v sl | sl P | | | O-O | NH.N‴ | 11 |
| 89 | Benzamide | $C_6H_5.CO.NH_2$ | sl | | | g | 18 J | | | F-O | $CONH_2$ | 6 |
| 90 | Benzamidine hydrochloride | $C_6H_5.C.NH.NH_2.HCl$ | v sol | | | | | | 33 C | O-O | NH, $NH_2$, $[Cl]^-$ | 6 |
| 91 | Benzanilid | $C_6H_5.CO.NH.C_6H_5$ | i | | | v sl | v sl P | | | O-O | CONH | 6 |
| 92 | Benzene azo diphenyl urea | $C_6H_5.N:N.N(CO.NH.C_6H_5)C_6H_5$ | i | | | | | | | O-O | N:N.NR, CONH | 15 |
| 93 | Benzene azo [α] naphthol | $C_6H_5.N:N.C_{10}H_6.OH$ | i | | | o | f P | o | o C | O-C | N:N, OH | 13 |
| 94 | Benzene azo [β] naphthol | $C_6H_5.N:N.C_{10}H_6.OH$ | i | | | o | v sl P | | | O-O | N:N, OH | 13 |
| 95 | Benzene azo resorcinol | $C_6H_5.N:N.C_6H_3(OH)_2$ | sl | o | −10 M | | | o | 35 M | O-C | N:N, OH | 8 |
| 96 | Benzene azo salicylic acid | $C_6H_5.N:N.C_6H_3(OH)COOH$ | 300 | sl | o M | | | o | 36 M | O-C | N:N, OH, COOH | 8 |
| 97 | Benzene diazo amino [p] toluene | $C_6H_5.N:N.NH.C_6H_4.CH_3$ | i | | | o | ex P | o | 50 C | O-C | N:N.NH | 11 |
| 98 | Benzene sulphochloride | $C_6H_5.SO_2Cl$ | i | | | f | 16 J | | | F-O | $SO_2Cl$ | 5 |
| 99 | Benzene sulphoamide | $C_6H_5.SO_2.NH_2$ | sl | f | −10 M | f | v sl P | o | o M | F-O | $SO_2$, $NH_2$ | 5 |
| 100 | Benzenyl amino thio phenol | [l] | i | | | v sl | v sl P | o | o C | O-O | N‴, S″ | 10 |
| 101 | Benzidine | $NH_2.C_6H_4.C_6H_4.NH_2$ | 9,400 | o | −12 M | v sl | 26 J | o | 67 M | O-C | $NH_2$ | 10 |
| 102 | Benzil | $C_6H_5.CO.CO.C_6H_5$ | i | o | o M | v sl | v sl P | o | o M | O-O | CO | 12 |
| 103 | Benzoic acid | $C_6H_5.COOH$ | 2,900 | g | o M | o | v sl J | o | o M | F-O | COOH | 6 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 104 | Benzoic anhydride | $(C_6H_5.CO)_2O$ | | | | v s | 26 J | | | O-O | CO, COC | 12 |
| 105 | Benzoin | $C_6H_5.CH(OH)CO.C_6H_5$ | i | sl | o M | f | v sl P, J | sl | o M | F-O | OH, CO | 12 |
| 106 | Benzophenone | $C_6H_5.CO.C_6H_5$ | i | | | f | o P, J | | | F-O | CO | 12 |
| 107 | Benzoyl chloride | $C_6H_5.COCl$ | d | | | sl | 33 J | | | O-O | COCl | 6 |
| 108 | Benzyl acetate | $CH_3.COO.CH_2.C_6H_5$ | v sl | | | g | 42 J | | | F-C | COO | 8 |
| 109 | Benzyl alcohol | $C_6H_5.CH_2.OH$ | 40,000 | | | g | v sl P | | | F-O | OH | 6 |
| 110 | Benzyl cyanide | $C_6H_5.CH_2.CN$ | i | | | f | f P | | | F-C | C:N | 7 |
| 111 | Benzyl diazo amino benzene | $C_6H_5.N:N.N(CH_2.C_6H_5).C_6H_5$ | i | | | | | o | 30 C | O-O | N:N.N | 17 |
| 112 | Benzyl mercaptan | $C_6H_5.CH_2.SH$ | v sl | | | f | f P | | | F-C | SH | 6 |
| 113 | Bismark brown | $(NH_2)_2:C_6H_3.N:N.C_6H_4.N:N.C_6H_3:(NH_2)_2.4HCl$ | sol | | | o | 58 P | | | O-C | N:N, $NH_2$ | 14 |
| 114 | Borneol | | v sl | | | g | o J | | | F-O | OH | 9 |
| 115 | Brom-acetanilid [p] | $CH_3.CO.NH.C_6H_4.Br$ | v sl | | | sl | 19 J | | | O-O | CONH | 6 |
| 116 | Brom-aniline [p] | $Br.C_6H_4.NH_2$ | i | | | f | 72 J | | | F-C | $NH_2$[n] | 5 |
| 117 | Brom-aniline hydrochloride [p] | $Br.C_6H_4.NH_2.HCl$ | sol | | | f | 74 J | | | F-C | [Cl]⁻$NH_2$[n] | 5 |
| 118 | Brom-benzene | $C_6H_5.Br$ | i | | | o | o P | | | O-O | None[n] | 6 |
| 119 | Bromo form | $CHBr_3$ | sl | | | o | o P | | | O-O | Br[n] | 0 |
| 120 | Brom-phenol [p] | $Br.C_6H_4.OH$ | sl | | | ex | 19 J | | | F-O | OH | 4 |
| 121 | Brom-toluene [p] | $Br.C_6H_4.CH_3$ | i | | | o | 18 J | | | O-O | None[n] | 7 |
| 122 | Brucine | ap | 3,100 | | | v sl | 58 J | | | O-C | N‴, CON‴, COC, OH | 18 |
| 123 | Butyl acetate | $CH_3.COO.C_4H_9$ | sl | | | g | v sl P | | | F-O | COO | 4 |
| 124 | Butyl alcohol | $CH_3(CH_2)_2.CH_2.OH$ | 83,000 | g | o M | f | v sl P | g | o M | F-O | OH | 3 |
| 125 | Butyl mercaptan | $CH_3(CH_2)_2CH_2.SH$ | i | | | f | f P | f | 55 C | F-C | SH | 3 |
| 126 | Butyl sulfide | $(C_4H_9)_2S$ | i | | | f | f P | | | F-C | S″ | 7 |
| 127 | Butyl sulfone | $(C_4H_9)_2SO_2$ | sl | | | f | C | | | F-O | $SO_2$ | 7 |
| 128 | Butyraldehyde | $CH_3(CH_2)_2CHO$ | 37,000 | | | f | o P | | | F-O | CO | 3 |
| 129 | Butyranilid | $C_3H_7.CO.NH.C_6H_5$ | sl | | | ex | 28 J | | | F-O | CONH | 8 |
| 130 | Butyric acid | $CH_3(CH_2)_2COOH$ | ∞ | g | sl M | | | o | 17 M | F-O | COOH | 3 |
| 131 | Caffeine | | 13,500 | g | 65 M | o | 37 M | f | 14 M | F-C | CON‴, N‴ | 4 |
| 132 | Caffeine citrate | $C_8H_{10}O_2N_4.COOH.CH_2.C(OH)COOH.CH_2.COOH$ | sol | | | sl | 37 J | | | O-C | CON‴, N‴, COOH, OH | 6 |
| 133 | Calcium benzoate | $(C_6H_5.COO)_2Ca$ | sl | g(p) | −10 M | o | o J | o | o M | O-O | COO | 6 |
| 134 | Calcium carbide | $CaC_2$ | d | o | o M | | | o | o M | O-O | None | 0 |
| 135 | Calcium formate | $(HCOO)_2Ca$ | 160,000 | | | o | o J | | | O-O | COO | 0 |
| 136 | Calcium lactate | $Ca(C_3H_5O_3)_2.5H_2O$ | 105,000 | o | o M | o | 19 J | o | o M | O-O | OH, COO | 1 |
| 137 | Calcium salicylate | $Ca(C_7H_5O_3)_2.2H_2O$ | v sol | | | o | o J | | | O-O | OH, COO | 4 |
| 138 | Camphor | " | v sol | ex | 44 M | g | 15 J | sl | 20 M | F-C | CO | 9 |
| 139 | Camphoric acid | " | 7,600 | ex | v sl M | o | o J | o | o M | F-O | COOH | 8 |
| 140 | Camphor sulfonic acid | " | sol | f | −23 M | f | 40 M | f | sl M | F-O | CO, $SO_3H$ | 8 |
| 141 | Capric acid | $CH_3(CH_2)_8.COOH$ | v sl | f | −50 M | f | 82 M | f | 35 M | F-C | COOH | 9 |
| 142 | Caproic acid | $CH_3(CH_2)_4COOH$ | v sl | | | f | sl P | | | F-O | COOH | 5 |
| 143 | Carbanilid | $C_6H_5.NH.CO.NH.C_6H_5$ | v sl | | | v sl | o P | | | O-O | CONH, NH | 11 |
| 144 | Carbazol | $C_6H_4.NH.C_6H_4$ | i | o | 25 M | o | 9 J | o | 7 M | O-O | NH | 10 |
| 145 | Carbothialdin | $NH_2.CS.S.N:(C_2H_4)_2$ | i | | | v sl | f P | f (t) | 66 C | O-C | $CSNH_2$, S″, N‴ | 3 |
| 146 | Carvacrol | $CH_3.C_6H_3(OH)CH(CH_3)_2$ | i | | | f | C | | | F-O | OH | 9 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[a] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Frothing | Collecting | Frothing | Collecting | Frothing | Collecting | | | |
| 147 | Carvacrylamine | $CH_3.CH.C_6H_2.CH_2.NH_2.OH$ | v sl | | | g | g P | g | 33 C | F-C | OH, $NH_2$ | 8 |
| 148 | Cetyl alcohol | $CH_3(CH_2)_{14}OH$ | i | | | o | o P | | | O-O | OH | 15 |
| 149 | Chlor-acetanilid [p] | $Cl.C_6H_4.NH.COCH_3$ | v sl | | | f | 25 J | | | F-O | $CONH^n$ | 6 |
| 150 | Chlor-acetic acid | $CH_2.Cl.COOH$ | v sol | o | o M | o | o J | o | o M | O-O | COOH, Cl | 0 |
| 151 | Chloral hydrate | $CCl_3.CH(OH)_2$ | 660,000 | f | o M | f | o P | o | o M | F-O | OH, Cl | 0 |
| 152 | Chlor-aniline [p] | $Cl.C_6H_4.NH_2$ | sl | | | f | 63 J | | | F-C | $NH_2$, Cl | 4 |
| 153 | Chlor-nitro-benzene [p] | $Cl.C_6H_4.NO_2$ | i | sl | 57 M | v sl | 19 J | sl | sl C | O-C | Cl, $NO_2$ | 4 |
| 154 | Chloroform | $CHCl_3$ | 6,200 | | | o | o P | | | O-O | Cl | 0 |
| 155 | Chlor-phenol [o] | $Cl.C_6H_4.OH$ | 28,500 | | | f | o P | | | F-O | $OH^n$ | 4 |
| 156 | Chlor-phenol [p] | $Cl.C_6H_4.OH$ | 27,100 | | | ex | 42 J | | | F-C | $OH^n$ | 4 |
| 157 | Chlortoluene [p] | $CH_3.C_6H_4.Cl$ | | | | v sl | 70 J | | | O-C | None[n] | 7 |
| 158 | Chrysene | u | v sl | | | o | o P | | | O-O | None | 18 |
| 159 | Chrysoidin | $C_6H_5.N:N.C_6H_3(NH_2)_2$ | sl | o | −15 M | v sl | g P | o | 79 M | O-C | N:N, $NH_2$ | 8 |
| 160 | Cinchonine | v | 270 | o | −48 M | o | o P | sl | 75 M | O-C | OH, N''' | 15 |
| 161 | Cinchonine sulfate | $(C_{19}H_{22}ON_2)_2H_2SO_4 + 2H_2O$ | 15,500 | | | o | 26 J | | | O-O | OH, N''',$[SO_4]^=$ | 15 |
| 162 | Cinchonidine sulfate | $(C_{19}H_{22}ON_2)_2.H_2SO_4 + 2H_2O$ | sol | | | o | 16 J | | | O-O | OH, N''', $[SO_4]^=$ | 15 |
| 163 | Cinnamic acid | $C_6H_5.CH:CH.COOH$ | 1,000 | f | −21 M | sl | o J | sl | 18 M | F-O | COOH | 8 |
| 164 | Citric acid | $COOH.CH_2.C(OH)(COOH)CH_2.COOH$ | 1,330,000 | o | 0 M | o | o C | o | o M | O-O | OH, COOH | 0 |
| 165 | Collodion | $(C_6H_{10}O_5)_x(NO_2)_3$ | i | o | o M | | | o | o M | O-O | $NO_2$ | 0 |
| 166 | Congo red | $NH_2(HSO_3)C_{10}H_5.N:N.C_6H_4.C_6H_4.N:N.C_{10}H_5(HSO_3)NH_2$ | sol | o | −37 M | | | o | −75 M | O-D | N:N, $NH_2$, $SO_3H$ | 24 |
| 167 | Coralline | h | v sl | f | −28 M | | | o | o M | F-O | h | h |
| 168 | Coumarin | aq | v sl | f | −23 M | ex | 32 J | o | o M | F-O | COO | 7 |
| 169 | Cresol [o] | $CH_3.C_6H_4.OH$ | 31,000 | g | o M | | | o | o M | F-O | OH | 6 |
| 170 | Cresol [p] | $CH_3.C_6H_4.OH$ | 23,600 | | | g | v sl P | | | F-O | OH | 6 |
| 171 | Crystal violet | $(CH_3)_2:N.C_6H_4.C[C_6H_4.N:(CH_3)_2].C_6H_4.N:(CH_3)_2.HCl$ | sol | o | −24 M | | | o | 63 M | O-C | N''', $[Cl]^-$ | 16 |
| 172 | Cuminol | $C_6H_4.C_3H_7.CH_2.OH$ | sl | | | f | sl P | | | F-O | OH | 9 |
| 173 | Dehydracet carboxylic acid | cr | sol | f | o M | o | −25 M | o | o M | F-O | COO, CO | 2 |
| 174 | Dehydro thiotoluidin [o] | w,as | i | | | o | f P | | 50 C | O-C | S'', N''' | 9 |
| 175 | Dehydro thiotoluidin [p] | w | i | | | o | g P | o | 25 C | O-C | S'', N''' | 9 |
| 176 | Dextrin | $(C_6H_{10}O_5)_x$ | c | o | −81 M | o | −84 M | o | −65 M | O-D | OH | 0 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 177 | Dextrose | at | 830,000 | o | −37 M | o | o M | o | o M | O-O | OH, CO | 0 |
| 178 | Diacetin | $C_3H_5(OH)(OOC.CH_3)_2$ | ■ | | | g | v sl P | | | F-O | OH, COO | 2 |
| 179 | Di-acetyl monoxime | $CH_3.CO.C(NOH)CH_3$ | sl | f | −42 M | f | o M | o | −41 M | F-D | CO, NOH | 2 |
| 180 | Di-acetyl succinic ester | $CH_3.CO.CH.COOH.CH_3.CO.CH.COOH$ | sl | f | sl M | | | o | sl M | F-O | CO, COOH | 4 |
| 181 | Di-amino phenyl disulfide | $NH_2.C_6H_4.S.S.C_6H_4.NH_2$ | v sl | | | sl | ex P | | | O-C | $NH_2$, S″ | 8 |
| 182 | Diazo amino benzene | $C_6H_5.N:N.NH.C_6H_5$ | 12 | o | 53 M | o | 77 M | o | 83 M | O-C | N:N.N | 10 |
| 183 | Diazo amino [p] toluene | $CH_3.C_6H_4.N:N.NH.C_6H_4.CH_3$ | i | | | o | ex P | o | 76 C | O-C | N:N.N | 11 |
| 184 | Diazo benzene imid (Phenyl azid) | $C_6H_5.N_3$ | v sl | | | | | o | o C | O-O | $N_3$ | 5 |
| 185 | Dibenzyl | $C_6H_5.CH_2.CH_2.C_6H_5$ | i | | | o | o P | | | O-O | None | 14 |
| 186 | Dibrom anthracene | au | i | | | o | o P | | | O-O | None$^n$ | 14 |
| 187 | Dibrom benzene | $C_6H_4.Br_2$ | i | | | o | o P | | | O-O | None$^n$ | 6 |
| 188 | Dichlor acetic acid | $CHCl_2.COOH$ | sol | o | o M | | | o | o M | O-O | Cl, COOH | 0 |
| 189 | Dichlor benzene | $C_6H_4.Cl_2$ | i | o | 56 M | | | o | 68 C | O-O | None$^n$ | 6 |
| 190 | Dicyan diamidine sulfate | $[HN:C(NH_2)NH.CO.NH_2]_2.H_2SO_4$ | sol | | | o | −12 J | | | O-O | NH, $CONH_2$, $NH_2$ | 0 |
| 191 | Diethylamine hydrochloride | $(C_2H_5)_2NH.HCl$ | v sol | o | −10 M | v sl | 11 J | g | 12 M | O-O | NH, $[Cl]^-$ | 3 |
| 192 | Diethyl dithio oxalate | $C_2H_5.S(CS)_2S.C_2H_5$ | v sl | | | | | o | 74 C | O-C | S″ | 4 |
| 193 | Diethyl ketone | $C_2H_5.CO.C_2H_5$ | sol | | | f | o P | | | F-O | CO | 4 |
| 194 | Diethyl thiourea | $C_2H_5.NH.CS.NH.C_2H_5$ | sl | | | o | o P | | | O-O | CSNH, NH | 2 |
| 195 | Diethyl sulfone dimethyl methane | $(C_2H_5)_2C(SO_2.CH_3)_2$ | sol | | | f | v sl P | | | F-O | $SO_2$ | 4 |
| 196 | Dimethylamine azo [p] toluene. | $CH_3.C_6H_4.N:N.N(CH_3)_2$ | i | | | | | o | 32 C | O-C | N:N.NR | 6 |
| 197 | Dimethylamine hydrochloride | $(CH_3)_2NH.HCl$ | v so | o | −7 M | | | o | 12 M | O-O | NH, $[Cl]^-$ | 1 |
| 198 | Dimethyl amino azo benzol | $C_6H_5.N:N.C_6H_4.N(CH_3)_2$ | v sl | o | −17 M | | | o | o M | O-O | N:N, N‴ | 10 |
| 199 | Dimethyl amino benzaldehyde [p] | $(CH_3)_2:N.C_6H_4.CHO$ | sol | g | o M | | | g | sl M | F-O | N‴, CO | 6 |
| 200 | Dimethyl aniline | $C_6H_4.N:(CH_3)_2$ | v sl | | | f | sl P | | | F-O | N‴ | 6 |
| 201 | Dimethyl diethyl pinacone | $OH.CH_3.C_2H_5.C.C_2H_5.CH_3.OH$ | sl | | | g | o P | | | F-O | OH | 6 |
| 202 | Dimethyl glyoxime | $(CH_3)_2.C_2(NOH)_2$ | i | g | −7 M | | | o | −22 M | O-O | NOH | 2 |
| 203 | Dimethyl toluidin [o] | $CH_3.C_6H_4.N:(CH_3)_2$ | sl | | | v sl | v sl P | | | O-O | N‴ | 7 |
| 204 | Dinaphthyl thio-urea | $C_{10}H_7.NH.CS.NH.C_{10}H_7$ | i | | | o | o P | | | O-O | CSNH, NH | 18 |
| 205 | Dinitrobenzene | $C_6H_4(NO_2)_2$ | 100 | o | o M | f | 70 J | g | o M | F-C | $NO_2$ | 4 |
| 206 | Dinitronaphthol | $(NO_2)_2.C_{10}H_5.OH$ | v sl | | | o | o P | | | O-O | $NO_2$, OH | 7 |
| 207 | Dinitrophenol (2, 4) | $(NO_2)_2.C_6H_3.OH$ | v sl | o | −30 M | | | o | −10 M | O-D | $NO_2$, OH | 4 |
| 208 | Dinitro-toluene | $(NO_2)_2.C_6H_3.CH_3$ | v sl | | | sl | sl P | | | O-O | $NO_2$ | 5 |
| 209 | Dioxyphenyl thiourea | $OH.C_6H_4.NH.CS.NH.C_6H_4.OH$ | v sl | | | o | sl P | | | O-O | OH, CSNH, NH | 8 |
| 210 | Diphenyl amine | $(C_6H_5)_2:NH$ | v sl | v sl | o M | o | 16 J | o | o M | O-O | NH | 11 |
| 211 | Diphenyl quanidine | $C_6H_5.NH.C.NH.C.NH.C_6H_5$ | i | f | −20 M | | | sl | 82 M | F-C | NH | 11 |
| 212 | Diphenyl oxide | $(C_6H_5)_2O$ | i | | | v sl | o P | | | O-O | COC | 11 |
| 213 | Diphenyl sulfone | $C_6H_5.SO_2.C_6H_5$ | i | sl | o M | | | o | o M | O-O | $SO_2$ | 11 |
| 214 | Diphenyl sulfoxide | $(C_6H_5)_2.SO$ | v sl | g | 50 M | | | g | o M | F-O | SO | 11 |
| 215 | Diphenyl thiocarbazid | $C_6H_5.NH.NH.CS.NH.NH.C_6H_5$ | i | | | o | g P | sl | 67 C | O-C | CSNH, NH | 10 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[e] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Frothing | Collecting | Frothing | Collecting | Frothing | Collecting | | | |
| 216 | Dithio diphenyl amine | $(C_6H_4.S.S.C_6H_4)_2$:NH | i | | | f | f P | | | F-C | NH, S″ | 8 |
| 217 | Dithio ethyl dimethyl methane | $(C_2H_5S)_2C(CH_3)_2$ | i | | | v sl | f P | | | O-C | S″ | 4 |
| 218 | Ditolyl [o] thiourea | $CH_3.C_6H_4.NH.CS.NH.C_6H_4.CH_3$ | i | | | o | ex P | o | 59 C | O-C | CSNH, NH | 12 |
| 219 | Ditolyl [p] thiourea | $CH_3.C_6H_4.NH.CS.NH.C_6H_4.CH_3$ | i | | | o | ex P | o | 93 C | O-C | CSNH, NH | 12 |
| 220 | Dixanthogen | $C_2H_5O.SC.S.CS.OC_2H_5$ | 2.3 | | | | | o | ex C | O-C | S″ | 4 |
| 221 | Dixylyl thiourea | $(CH_3)_2C_6H_3.NH.CS.NH.C_6H_3(CH_3)_2$ | i | | | o | ex P | o | 50 C | O-C | CSNH, NH | 14 |
| 222 | Eosine | *av* | i | o | −22 M | v sl | −67 J | o | 19M | O-D | COC, OH, COO | 13 |
| 223 | Erythritol | $(CH_2.OH.CH.OH)_2$ | v sol | o | −26 M | o | o M | o | o M | O-O | OH | 0 |
| 224 | Ethyl acetanilid | $C_6H_5.N(C_2H_5)COCH_3$ | i | f | o M | f | o M | f | o M | F-O | CON‴ | 8 |
| 225 | Ethyl acetate | $CH_3.COOC_2H_5$ | 86,000 | g | o M | f | o P | f | o M | F-O | COO | 2 |
| 226 | Ethyl amine | $C_2H_5.NH_2$ | ∞ | o | −35 M | o | 27 M | o | 14 M | O-O | $NH_2$ | 1 |
| 227 | Ethylamine hydrochloride | $C_2H_5.NH_2.HCl$ | v sol | | | o | 16 M | | | O-O | $NH_2$, $[Cl]^-$ | 1 |
| 228 | Ethyl [p] amino benzoate | $NH_2.C_6H_4.COO.C_2H_5$ | sl | f | 33 M | f | 49 M | f | 17 M | F-C | $NH_2$, COO | 6 |
| 229 | Ethyl ethyl xanthate | $C_2H_5O.CS.S.C_2H_5$ | i | | | | | o | f C | O-C | S″ | 4 |
| 230 | Ethyl methyl xanthate | $C_2H_5O.CS.S.CH_3$ | v sl | | | | | o | g C | O-C | S″ | 3 |
| 231 | Ethyl [m] nitrobenzoate | $NO_2.C_6H_4.COO.C_2H_5$ | i | | | sl | 39 J | | | O-C | $NO_2$, COO | 7 |
| 232 | Ethyl [p] nitrobenzoate | $NO_2.C_6H_4.COO.C_2H_5$ | i | | | g | 39 J | | | F-C | $NO_2$, COO | 7 |
| 233 | Ethyl carbonate | $(C_2H_5)_2CO_3$ | i | | | f | o P | | | F-O | COO | 4 |
| 234 | Ethyl malonic acid | $C_2H_5.CH(COOH)_2$ | sol | | | g | sl P | | | F-O | COOH | 3 |
| 235 | Ethyl sulfide | $(C_2H_5)_2S$ | i | | | o | o P | | | O-O | S″ | 3 |
| 236 | Ethylene diacetate | $COCH_3.O.CH:CH.O.COCH_3$ | sl | | | g | sl P | | | F-O | COO | 4 |
| 237 | Eucalyptol | *aw* | i | | | g | sl P | | | F-O | OH, COC | 8 |
| 238 | Fluorene | $(C_6H_4)_2CH_2$ | i | o | o M | o | sl M | o | o M | O-O | None | 13 |
| 239 | Fluorescein | *ay* | i | o | −35 M | o | 14 M | o | −20 M | O-O | COC, OH, COO | 13 |
| 240 | Formaldehyde | HCHO | sol | o | −15 M | o | sl M | o | o M | O-O | CO | 0 |
| 241 | Formamide | $HCONH_2$ | ∞ | o | o M | o | o M | o | sl M | O-O | $CONH_2$ | 0 |
| 242 | Formanilid | $HCO.NH.C_6H_5$ | sol | f | −18 M | f | sl P | f | o M | F-O | CONH | 5 |
| 243 | Formazyl azobenzene | $(C_6H_5.N:N)_2C:N.NH.C_6H_5$ | i | | | o | f P | | | O-C | N:N, N‴, NH | 15 |
| 244 | Formic acid | HCOOH | ∞ | o | o M | | | o | o M | O-O | COOH | 0 |
| 245 | Fumaric acid | COOH.CH:CH.COOH | 7,000 | | | o | o J | | | O-O | COOH | 2 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 246 | Galactose | *at* | v sol | o | −30 M | o | o M, J | o | −45 M | O-D | OH, CO | 0 |
| 247 | Galactose pentacetate | *as* | i | | | g | o P | | | F-O | COC, CO | 5 |
| 248 | Gallic acid | $(HO)_3C_6H_2.COOH$ | 11,600 | o | −60 M | o | −57 M | o | −24 M | O-D | COOH, OH | 3 |
| 249 | Gelatine | Protein[h] | C | o | −67 M | o | −77 M | o | −62 M | O-D | | |
| 250 | Glucosazone | | v s | o | o M | | | f | 47 M | F-C | N‴, NH, OH | 12 |
| 251 | Glucose pentacetate | *as* | v sl | | | g | o P | | | F-O | COC, CO | 5 |
| 252 | Glucose phenyl hydrazone | *ba* | v sol | | | v sl | sl P | | | O-O | N‴, NH, OH | 5 |
| 253 | Glutamic acid | $C_3H_5(NH_2)(COOH)_2$ | 10,000 | o | −30 M | o | −70 M | o | −31 M | O-D | NH, COOH | 2 |
| 254 | Glutaric acid | $COOH(CH_2)_3COOH$ | 670,000 | f | −17 M | o | o M | o | o M | O-O | COOH | 2 |
| 255 | Glycerin | $CH_2.OH.CH.OH.CH_2.OH$ | ∞ | o | o M | | | o | o M | O-O | OH | 0 |
| 256 | Glycol | $OH.CH_2.CH_2.OH$ | ∞ | o | o M | sl | o P | o | o M | O-O | OH | 0 |
| 257 | Guiacol | $HO.C_6H_4.OCH_3$[o] | 16,000 | | | f | o P | | | F-O | COC, OH | 5 |
| 258 | H-acid | $(SO_3H)_2.C_{10}H_3.OH.NH_2$.Acid | sol | o | −21 M | | | o | o M | O-O | $SO_3H$, OH, $NH_2$ | 6 |
| 259 | Hematoxylin | $C_{16}H_{14}O_6 + 3H_2O$[h] | v sl | o | o M | o | −80 M | o | −55 M | O-D | h | h |
| 260 | Heptyl mercaptan | $CH_3(CH_2)_6SH$ | v sl | | | | | o | 63 C | O-C | SH | 6 |
| 261 | Heptyl sulfide | $[CH_3(CH_2)_6]_2S$ | v sl | | | | | o | o C | O-O | S″ | 13 |
| 262 | Hexachlor ethane | $CCl_3.CCl_3$ | i | | | o | o J | | | O-O | Cl | 0 |
| 263 | Hexamethylene tetramine | $(CH_2)_6N_4$ | 830,000 | o | −14 M | o | 24 M | o | −31 M | O-O | NH, N‴ | 0 |
| 264 | Hippuric acid | $C_6H_5.CO.NH.CH_2.COOH$ | 330,000 | f | −25 M | f | sl M | o | o M | F-O | CONH, COOH | 7 |
| 265 | Homosalicyl aldehyde [p] | $CH_3.C_6H_3(OH)CHO$ | sl | f | o M | f | 14 M | f | 9 M | F-O | OH, CO | 7 |
| 266 | Hydrazine sulfate | $NH_2.NH_2.H_2SO_4$ | sol | | | o | 30 J | | | O-O | $NH_2$, $[SO_4]^-$ | 0 |
| 267 | Hydrazobenzene | $C_6H_5.NH.NH.C_6H_5$ | v sl | o | o M | o | f P | o | 21 M | O-C | NH | 10 |
| 268 | Hydrocinnamic acid | $C_6H_5.CH_2.CH_2.COOH$ | 5,900 | g | o M | | | g | sl M | F-O | COOH | 8 |
| 269 | Hydroquinone | $C_6H_4(OH)_2$ | 590,000 | sl | o M | v sl | o M | o | −44 M | O-O | OH | 4 |
| 270 | Hydroxy azobenzene | $C_6H_5.N:N.C_6H_4.OH$ | v sl | | | | | sl | o C | O-O | N:N, OH | 9 |
| 271 | Hydroxylamine | $NH_2.OH$ | sol | | | v sl | v sl P | | | O-O | $NH_2$, OH | 0 |
| 271a | Hydroxylamine hydrochloride | $NH_2.OH.HCl$ | v sol | o | o M | | | o | o M | O-O | $NH_2$, OH, $[Cl]^-$ | 0 |
| 272 | Indigotin | *z* | ∞ | o | −10 M | o | o P | o | o M | O-O | CONH | 8 |
| 273 | Inulin | $(C_{16}H_{10}O_5)_x$[h] | 10, C | o | −26 M | o | −53 M | o | −35 M | O-D | h | h |
| 274 | Iodoform | $CH_3I$ | 100 | | | v sl | 58 M | | | O-C | None | 1 |
| 275 | Isatin | *y* | v sl | f | −12 M | o | o M | f | sl M | F-O | CONH, CO | 5 |
| 276 | Isopropyl acetate | $CH_3.COO.CH(CH_3)_2$ | sl | | | g | o P | | | F-O | COO | 4 |
| 277 | Isovaleraldehyde | $(CH_3)_2.CH.CH_2.CHO$ | sl | | | v sl | o P | | | O-O | CO | 4 |
| 278 | Lactic acid | $CH_3.CH(OH).COOH$ | ∞ | g | o M | o | sl M | o | o M | F-O | COOH, OH | 1 |
| 279 | Lactose | *bc* | 170,000 | o | o M | o | o M | o | o M | O-O | OH, CO, COC | 0 |
| 280 | Lauric acid | $C_{11}H_{23}.COOH$ | i | o | −33 M | o | 67 M | o | 29 M | O-C | COOH | 11 |
| 281 | Laurome | $C_{11}H_{23}.CO.C_{11}H_{23}$ | i | o | o M | o | o M | o | o M | O-O | CO | 22 |
| 282 | Lead dithiofuroate | *s* | i | | | | | o | o C | O-O | S″, SM, COC | 2 |
| 283 | Lepidine | *aa* | v sl | f | o M | f | 27 M | f | 73 M | F-C | N‴ | 8 |
| 284 | Leucine 1 | $CH_3(CH_2)_3CH(NH_2).COOH$ | 24,000 | f | o M | o | −77 M | f | −50 M | F-D | COOH, $NH_2$ | 4 |
| 285 | Levulose | $CH_2(OH)(CHOH)_3CO.CH_2OH$ | v sol | | | o | o J | | | O-O | OH, CO | 0 |
| 286 | Magenta | $NH_2.C_6H_4.C(C_6H_3.CH_3.NH_2,C_6H_3.NH_2.Cl$ | v sl | o | −45 M | o | −81 J | o | 42 M | O-D | $NH_2$, Cl | 10 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[a] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Frothing | Collecting | Frothing | Collecting | Frothing | Collecting | | | |
| 287 | Magnesium acetate | $(CH_3.COO)_2Mg$ | sol | f | o M | | −J | o | −6 M | F-O | COO | 2 |
| 288 | Malachite green | $NH_2.C_6H_4(C_6H_4.NH_2)C_6H_4:NH.HCl$ | sol | o | −13 M | o | −60 M | o | 83 M | O-C | $NH_2$, NH, $[Cl]^-$ | 14 |
| 289 | Maleic acid | COOH.CH:CH.COOH | 788,000 | o | o M | o | o J | o | o M | O-O | COOH | 2 |
| 290 | Malic acid | $COOH.CH_2.CH(OH)COOH$ | v sol | o | −26 M | o | −43 M | o | 35 M | O-D | COOH, OH | 1 |
| 291 | Malonic acid | $CH_2(COOH)_2$ | +1,000,000 | o | o M | o | o M | o | o M | O-O | COOH | 1 |
| 292 | Malonic amide | $CH_2(CONH_2)_2$ | 83,000 | o | o M | o | o M | o | o M | O-O | $CONH_2$ | 1 |
| 293 | Maltose | [bc] | v sol | o | o M | o | −74 J | o | o M | O-D | OH, CO, COC | 0 |
| 294 | Mandelic acid | $C_6H_5.CH(OH)COOH$ | 160,000 | f | −6 M | | | o | o M | F-O | COOH, OH | 6 |
| 295 | Mannite | $CH_2.OH(CH.OH)_4.CH_2OH$ | v sol | | | o | o P | | | O-O | OH | 0 |
| 296 | Menthol | [ab] | sl | f | o M | | | sl | sl M | F-O | OH | 9 |
| 297 | Mesityl oxide | $(CH_3)_2C:CH.COCH_3$ | i | | | ex | o P | | | F-O | CO | 5 |
| 298 | Metaldehyde | $(C_2H_4O)_4$ | i | | | g | o P | | | F-O | CO | 8 |
| 299 | Methyl acetate | $CH_3.COO.CH_3$ | 319,000 | o | o M | | | o | o M | O-O | COO | 1 |
| 300 | Methyl acetoacetic acid | $CH_3.CO.CH(CH_3).COOH$ | v sl | | | f | sl P | | | F-O | CO, COOH | 3 |
| 301 | Methyl alcohol | $CH_3.OH$ | ∞ | o | o M | | | o | o M | O-O | OH | 0 |
| 302 | Methyl amine | $CH_3.NH_2$ | v sol | | | o | o P | | | O-O | $NH_2$ | 0 |
| 303 | Methyl amine hydrochloride | $CH_3.NH_2.HCl$ | v sol | o | −8 M | v sl | −14 J | o | 22 M | O-O | $NH_2$, $[Cl]^-$ | 0 |
| 304 | Methyl aminophenol sulfate [o]. | $CH_3.NH.C_6H_4.OH.H_2SO_4$ | sol | | | f | 46 J | | | F-C | NH, OH, $[SO_4]^=$ | 5 |
| 305 | Methyl diazoaminobenzene | $C_6H_5.N:N.N(CH_3).C_6H_5$ | i | | | | | o | 25 C | O-O | N:N, N''' | 11 |
| 306 | Methyl orange | $(CH_3)_2.N.C_6H_4.N:N.C_6H_4.SO_3H$ | sl | o | −17 M | | | f | 18 M | F-O | N:N, N''', $SO_3H$ | 10 |
| 307 | Methyl red | $(CH_3)_2.N.C_6H_4.N:N.C_6H_4.COOH$ | sl | o | −13 M | | | g | 56 M | F-C | N:N, N''', COOH | 10 |
| 308 | Methyl violet | $(CH_3)_2N.C_6H_4.C[C_6H_4.N(CH_3)_2]:C_6H_4:N.CH_3.HCl$ | sol | o | −33 M | | | f | 60 M | F-C | N''', $[Cl]^-$ | 12 |
| 309 | Methylene blue | [ac] | sol | o | −22 M | o | 35 J | o | 16 M | O-C | NH, N''', S'', $NH_2$ | 9 |
| 310 | Metol | $CH_3.NH.C_6H_4.OH.H_2SO_4$ | v sol | | | v sl | v sl P | | | O-O | OH, NH, $[SO_4]^=$ | 4 |
| 311 | Monoacetin | $CH_2(OH)CH(OH).CH_2.OOC.CH_3$ | v sol | | | g | sl P | | | F-O | OH, COO | 1 |
| 312 | Mucic acid | $COOH(CHOH)_4COOH$ | 3,300 | o | o M | o | 33 J | o | −23 M | O-O | COOH, OH | 0 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 313 | Naphthalene | ad | | o | o M | o | o P | o | o M | O-O | None | 10 |
| 314 | Naphthalene azonaphthol | $C_{10}H_7.N:NC_{10}H_6.OH$ | i | | | v sl | g P | | | O-C | N:N, OH | 17 |
| 315 | Naphthoic acid | $C_{10}H_7.COOH$ | v sl | | | v sl | v sl P | | | O-O | COOH | 9 |
| 316 | Naphthol [α] | $C_{10}H_7.OH$ | i | g | o M | g | 23 J | sl | 22 M | F-O | OH | 9 |
| 317 | Naphthol [β] | $C_{10}H_7.OH$ | sl | g | o M | g | 19 J | sl | 12 M | F-O | OH | 9 |
| 318 | Naphthol sulfonic acid | $C_{10}H_6(OH)SO_3H$ | sol | | | v sl | v sl P | | | O-O | OH, $SO_3H$ | 8 |
| 319 | Naphthyl hydrazine [α] | $C_{10}H_7.NH.NH_2$ | v sl | | | v sl | g P | | | O-C | NH, $NH_2$ | 9 |
| 320 | α-Naphthyl β-hydroxylamine | $C_{10}H_7.NH.OH$ | sl | | | v sl | f P | | | O-C | NH, OH | 9 |
| 321 | Naphthyl iso thio cyanate | $C_{10}H_7.N:C:S$ | v sl | | | o | o P | | | O-O | NCS | 9 |
| 322 | Naphthylamine [α] | $C_{10}H_7.NH_2$ | 1,700 | sl | o M | f | 79 J | f | 76 M | F-C | $NH_2$ | 9 |
| 323 | Naphthylamine [β] | $C_{10}H_7.NH_2$ | sl | | | f | 79 J | | | F-C | $NH_2$ | 9 |
| 324 | Naphthylamine sulfonic acid | $NH_2.C_{10}H_6.SO_3H + \frac{1}{2}H_2O$ | 200 | | | v sl | v sl P | | | O-O | $NH_2$, $SO_3H$ | 8 |
| 325 | Nicotine | ae | ∞ | | • | sl | sl P | | | O-O | N''' | 8 |
| 326 | Nitraniline [m] | $NO_2.C_6H_4.NH_2$ | sl | | | v sl | 72 J | | | O-C | $NO_2$, $NH_2$ | 4 |
| 327 | Nitraniline [o] | $NO_2.C_6H_4.NH_2$ | v sl | o | −20 M | sl | v sl P | f | 39 M | F-C | $NO_2$, $NH_2$ | 4 |
| 328 | Nitraniline [p] | $NO_2.C_6H_4.NH_2$ | 800 | | | sl | −50 J | | | O-D | $NO_2$, $NH_2$ | 4 |
| 329 | Nitroacetanilid [p] | $NO_2.C_6H_4.NH.CO.CH_3$ | sl | | | g | 33 J | | | F-C | $NO_2$, CONH | 4 |
| 330 | Nitroanisole [p] | $NO_2.C_6H_4.OCH_3$ | v sl | | | f | 42 J | | | F-C | $NO_2$, COC | 4 |
| 331 | Nitrobenzaldehyde [m] | $NO_2.C_6H_4.CHO$ | v sl | | | g | 58 J | | | F-C | $NO_2$, CO | 4 |
| 332 | Nitrobenzaldehyde [o] | $NO_2.C_6H_4.CHO$ | v sl | | | g | 28 J | | | F-O | $NO_2$, CO | 4 |
| 333 | Nitrobenzene | $C_6H_5.NO_2$ | v sl | | | v sl | v sl P | f | 80 C | F-C | $NO_2$ | 5 |
| 334 | Nitrobenzoic acid [m] | $NO_2.C_6H_4.COOH$ | 3,100 | | | sl | 18 J | | | O-O | $NO_2$, COOH | 4 |
| 335 | Nitrobenzoic acid [o] | $NO_2.C_6H_4.COOH$ | 6,800 | | | v sl | 16 J | | | O-O | $NO_2$, COOH | 4 |
| 336 | Nitrobenzoic acid [p] | $NO_2.C_6H_4.COOH$ | 400 | | | sl | 25 J | | | O-O | $NO_2$, COOH | 4 |
| 337 | Nitrobrom benzene [p] | $NO_2.C_6H_4.Br$ | i | | | v sl | 26 J | | | O-O | $NO_2$, Br | 4 |
| 338 | Nitrocymene | $NO_2(CH_3)C_6H_3.CH(CH_3)_2$ | v sl | | | g | v sl P | | | F-O | $NO_2$ | 8 |
| 339 | Nitronaphthalene [α] | $C_{10}H_7.NO_2$ | i | o | o M | sl | 63 M | sl | o M | O-C | $NO_2$ | 9 |
| 340 | Nitrophenol [m] | $NO_2.C_6H_4.OH$ | sl | o | −14 M | | | o | o M | O-O | $NO_2$, OH | 4 |
| 341 | Nitrophenol [o] | $NO_2.C_6H_4.OH$ | v sl | o | −14 M | v sl | 19 M | o | o M | O-O | $NO_2$, OH | 4 |
| 342 | Nitrophenol [p] | $NO_2.C_6H_4OH$ | sl | o | −17 M | f | 25 J | o | o M | O-O | $NO_2$, OH | 4 |
| 343 | Nitrophenyl hydrazine [p] | $NO_2.C_6H_4.NH.NH_2$ | v sl | | | v sl | v sl P | | | O-O | $NO_2$, NH, $NH_2$ | 4 |
| 344 | Nitrotoluene [o] | $NO_2.C_6H_4CH_3$ | v sl | | | v sl | v sl P | | | O-O | $NO_2$ | 5 |
| 345 | Nitrotoluene [p] | $NO_2.C_6H_4.CH_3$ | v sl | | | f | 42 J | | | F-C | $NO_2$ | 5 |
| 346 | Nitrotoluidin [3, 1, 4] | $NO_2.C_6H_3.(CH_3)NH_2$ | v sl | | | sl | sl P | | | O-O | $NO_2$, $NH_2$ | 5 |
| 347 | Nitroso dimethyl aniline | $NO.C_6H_4.N(CH_3)_2$ | v sl | | | o | o P | | | O-O | NO, N''' | 4 |
| 348 | Nitroso [β] naphthol | $NO.C_{10}H_6.OH$ | v sl | o | o M | v sl | v sl P | sl | 41 M | O-C | NO, OH | 8 |
| 349 | Nitroso phenol [p] | $NO.C_6H_4.OH$ | sol | | | v sl | v sl P | | | O-O | NO, OH | 6 |
| 350 | Oenanthol | $C_6H_{13}.CHO$ | 1,200 | | | f | o P | | | F-O | CO | 6 |
| 351 | Orange I [α] naphthol | $HSO_3.C_6H_4.N:N.C_{10}H_5.OH$ (Na salt) | sol | o | −12 M | ex | −79 J | o | 12 M | F-D | N:N, OH, $SO_3H$ | 12 |
| 352 | Orcin | $CH_3.C_6H_3(OH)_2$ | v sol | | | g | v sl P | | | F-O | OH | 5 |
| 353 | Oxalic acid | $(COOH)_2 + 2H_2O$ | 95,000 | o | o M | | | o | o M | O-O | COOH | 0 |
| 354 | Oxyazobenzene | $OH.C_6H_4.N:N.C_6H_5$ | sl | | | sl | f P | | | O-C | N:N, OH | 9 |
| 355 | Palmitic acid | $CH_3.(CH_2)_{14}.COOH$ | i | | | o | 12 J | | | O-O | COOH | 15 |
| 356 | Paraformaldehyde | $(CH_2O)_x$ | v sol | | | o | o J | | | O-O | CO | 0 |
| 357 | Paradol | $(C_4H_8O_2)_2$ | v sl | | | f | o P | | | F-O | CO | [illegible] |
| 358 | Phenanthrene | bd | i | o | 10 M | o | 9 J | o | 13 M | O-O | None | 14 |
| 359 | Phenetedin [o] | $C_2H_5.O.C_6H_4.NH_2$ | v sl | | | g | v sl P | | | F-O | COC, $NH_2$ | 6 |
| 360 | Phenetedin [p] | $C_2H_5.O.C_6H_4.NH_2$ | v sl | | | f | g P | | | F-C | COC, $NH_2$ | 6 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water Parts per Million[d] | Results of Flotation Tests[e] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Frothing | Collecting | Frothing | Collecting | Frothing | Collecting | | | |
| 361 | Phenetol | $C_6H_5.OC_2H_5$ | i | | | g | 58 J | | | F-C | COC | 7 |
| 362 | Phenol | $C_6H_5.OH$ | 60,000 | g | o M | | | o | o M | F-O | OH | 5 |
| 363 | Phenyl ammonium thiuram disulfide. | $C_6H_5.N:C(S.NH_4)S_2.CS.NH_4.C_6H_5$ | v sl | | | f | f P | | | F-C | N‴, CSNH, S″, SM | 10 |
| 364 | Phenyl azoformazyl | $(C_6H_5.N:N)_2C:N.NH.C_6H_5$ | v sl | | | v sl | f P | | | O-C | N:N, N‴, NH | 15 |
| 365 | Phenyl benzoate | $C_6H_5.COO.C_6H_5$ | v sl | | | o | 16 J | | | O-O | COO | 11 |
| 366 | Phenyl ethyl thiourea | $C_6H_5.NH.CS.NH.C_2H_5$ | 174 | | | | | g | 95 C | F-C | CSNH, NH | 7 |
| 367 | Phenyl hydrazine | $C_6H_5.NH.NH_2$ | sl | | | f | ex P | | | F-C | NH, $NH_2$ | 5 |
| 368 | Phenyl hydrazine hydrochloride | $C_6H_5.NH.NH_2.HCl$ | sol | | | f | 84 J | | | F-C | NH, $NH_2$, $[Cl]^-$ | 5 |
| 369 | Phenyl hydroxylamine | $C_6H_5.NH.OH$ | 20,000 | | | sl | f P | | | O-C | NH, OH | 5 |
| 370 | Phenyl isothiocyanate | $C_6H_5.N:C:S$ | v sl, d | | | v sl | f P | sl | 50 C | O-C | NCS | 5 |
| 371 | Phenyl naphthylamine [α] | $C_{10}H_7.NH.C_6H_5$ | i | | | v sl | v sl P | | | O-O | NH | 15 |
| 372 | Phenyl salicylate | $HO.C_6H_4.COO.C_6H_5$ | v sl | sl | (t) 78 C | o | 25 M | o | o M | O-O | OH, COO | 9 |
| 373 | Phenyl thiohydantoic acid | $C_6H_5.NH.CS.NH.CH_2.COOH$ | sl | | | | | sl | 60 C | O-C | CSNH, COOH | 6 |
| 374 | Phenyl thiourea | $C_6H_5.NH.NH_2$ | 2,400 | | | v sl | ex P | sl | 67 C | O-C | CSNH, $NH_2$ | 5 |
| 375 | Phenyl thiourethane | $C_6H_5.NH.SC.OC_2H_5$ | v sl | | | | | o | 81 C | O-C | CSNH, COC | 7 |
| 376 | Phenyl urea | $C_6H_5.NH.CO.NH_2$ | sl | | | f | 16 J | | | F-O | CONH, $NH_2$ | 5 |
| 377 | Phenyl urethane | $C_6H_5.NH.COO.C_2H_5$ | v sl | | | ex | o J | | | F-O | CONH, COO | 7 |
| 378 | Phenylene diamine [m] | $C_6H_4(NH_2)_2$ | sol | | | sl | sl P | | | O-O | $NH_2$ | 4 |
| 379 | Phenylene diamine [p] | $C_6H_4(NH_2)_2$ | sol | | | v sl | v sl P | | | O-O | $NH_2$ | 4 |
| 380 | Phenylene diamine hydrochloride [m] | $C_6H_4(NH_2)_2.HCl$ | sol | o | −16 M | | | sl | 51 M | O-C | $NH_2$, $[Cl]^-$ | 4 |
| 381 | Phenylene diamine hydrochloride [p] | $C_6H_4(NH_2)_2.HCl$ | sol | o | −12 M | | | sl | 12 M | O-O | $NH_2$, $[Cl]^-$ | 4 |
| 382 | Phorone | $(CH_3)_2.C_6H_2.O_2$ | sl | | | ex | o P | | | F-O | CO | 7 |
| 383 | Phthalimid | $C_6H_4(CO)_2NH$ | v sl | | | g | 23 J | | | F-O | CONH, CO | 6 |
| 384 | Phthallic acid | $C_6H_4(COOH)_2$ [o] | 5,400 | | | o | 12 J | | | O-O | COOH | 6 |
| 385 | Phthallic anhydride | $C_6H_4(CO)_2O$ | v sl | f | o M | v sl | 11 J | o | o M | O-O | CO, COC | 6 |
| 386 | Picric acid | $(NO_2)_3.C_6H_2.OH$ | 12,200 | o | o M | v sl | 9 J | o | −14 M | O-O | $NO_2$, OH | 2 |
| 387 | Pinacoline | $CH_3.CO.C(CH_3)_3$ | v sl | | | o | o P | | | O-O | CO | 5 |
| 388 | Pinacone | $(CH_3)_2C(OH)C(OH)(CH_3)_2$ | sol | | | ex | 39 J | | | F-C | OH | 4 |
| 389 | Pinacone hydrate | $(CH_3)_2C(OH)C(OH)(CH_3)_2.H_2O$ | sl | | | g | o P | | | F-O | OH | 4 |
| 390 | Piperidine | *be* | ∞ | | | v sl | v sl P | | | O-O | NH | 3 |
| 391 | Piperine | *af* | v sl | | | v sl | 46 J | | | O-C | CO, N‴, COC | 13 |
| 392 | Piperonal | $CH_2.O_2.C_6H_3.CHO$ | 2,000 | | | v sl | o P | | | O-O | COC, CO | 5 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 393 | Potassium acid oxalate | $KHC_2HO_4$ | sol | | | o | 15 J | | | O-O | $[COO]^-$ | 0 |
| 394 | Potassium amyl sulphate | $K.C_5H_{11}.SO_4$ | sol | | | ex | 33 J | | | F-O | $[SO_4]$ | 4 |
| 395 | Potassium bitartrate | $KH.C_4H_4O_6$ | 6,000 | | | o | 19 | o | o C | O-O | COOH, $[COO]^-$ | 0 |
| 396 | Potassium dithio oxalate | KO.CS.CS.OK | sol | | | | | o | o C | O-O | S'', SM | 0 |
| 397 | Potassium ethyl sulfate | $K.C_2H_5.SO_4$ | sol | o | o M | o | o J | o | o M | O-O | $[SO_4]^-$ | 1 |
| 398 | Potassium hydrogen phthalate | $C_6H_4.C_2O_4HK$ | sl | f | −13 M | | | o | o M | F-O | COOH, $[COO]^-$ | 6 |
| 399 | Potassium salicylate | $C_6H_4.OH.COO.K$ | sol | | | o | 29 M | f | 52 C | F-C | $[COO]^-$, OH | 5 |
| 400 | Potassium xanthate | $C_2H_5O.CS.SK$ | v sol | | | | | o | 95 C | O-C | S'', SM, COC | 2 |
| 401 | Propionic acid | $CH_3.CH_2.COOH$ | ∞ | g | o M | f | o P | o | o M | F-O | COOH | 2 |
| 402 | Pseudocumidine | $(CH_3)_3.C_6H_2.NH_2$ | sl | | | f | f P | | | F-C | $NH_2$ | 8 |
| 403 | Pyridine | [aq] | ∞ | | | f | 65 J | | | F-C | N''' | 4 |
| 404 | Pyrocatechin | $C_6H_4(OH)_2$ [o] | v sol | f | −10 M | o | −50 J | o | −45 M | O-D | OH | 4 |
| 405 | Pyrogallol | $C_6H_3(OH)_3$ | v sol | o | o M | o | −84 J | o | −50 M | O-D | OH | 3 |
| 406 | Quinaldine | [ah] | v sl | | | g | f P | | | F-C | N''' | 9 |
| 407 | Quinine hydrobromide | [ai] | sol | | | o | −14 P | | | O-O | N''', OH, COC, $[Br]^-$ | 16 |
| 408 | Quinoline | [bf] | sl | | | ex | 54 J | | | F-C | N''' | 7 |
| 409 | Quinoline hydrochloride | $C_9H_7NHCl$ | sol | o | −13 M | | | g | 81 M | F-C | N''', $[Cl]^-$ | 8 |
| 410 | Quinoline salicylate[aj] | $C_9H_7NC_6H_4(OH)$-(COOH) | sl | | | f | f P | | | F-C | N''', COOH, OH | 11 |
| 411 | Quinone | $C_6H_4.O_2$ | sl | sl | o M | o | o J | o | −20 M | O-O | CO | 4 |
| 412 | Resorcinol | $C_6H_4(OH)_2$ [m] | v sol | g | o M | f | o J | o | −58 M | F-O | OH | 4 |
| 413 | Rosaniline | $C(OH)(CH_3.C_6H_3.NH_2)(C_6H_4.NH_2)_2$ | sl | o | −30 M | | | o | 45 M | O-C | $NH_2$, OH | 8 |
| 414 | Salicylic acid | $OH.C_6H_4.COOH$ | 2,700 | g | sl C | o | 24 J | o | o M | F-O | COOH, OH | 5 |
| 415 | Seleno benzamid | $C_6H_5.CSe.NH_2$ | v sl | | | | | o | 33 C | O-C | CSeNH | 6 |
| 416 | Semi-carbazid hydrochloride | $NH_2.CO.NH.CO.NH_2.HCl$ | sol | | | o | −10 J | | | O-O | NH, $NH_2$, CO, $[Cl]^-$ | 0 |
| 417 | Sodium acetate | $CH_3.COO.Na$ | 1,110,000 | f | o M | | | o | o M | F-O | $[COO]^-$ | 1 |
| 418 | Sodium alizarin sulfonate | $C_6H_4(CO)_2C_6H(OH)_2.SO_3Na$ | sol | sl | −20 M | | | o | −70 M | O-D | $SO_3M$, OH, CO | 9 |
| 419 | Sodium benzene sulfonate | $C_6H_5.SO_3Na$ | v sol | o | −9 M | | | o | o M | O-O | $SO_3M$ | 5 |
| 420 | Sodium citrate | $2[COO.Na.CH_2.C(OH)(COO.Na).CH_2.COO.Na].11\ H_2O$ | 910,000 | o | o M | | | o | o M | O-O | $[COO]^-$, OH | 2 |
| 421 | Sodium dithiophenyl carbamate | $C_6H_5.NH.CS.SNa$ | sol | | | | | o | 50 C | O-C | CSNH', SM | 6 |
| 422 | Sodium ethylate | $C_2H_5O.Na$ | d | sl | o M | | | o | o M | O-O | OM | 1 |
| 423 | Sodium formate | $HCOO.Na$ | 440,000 | sl | o M | | | o | o M | O-O | $[COO]^-$ | 0 |
| 424 | Sodium oxalate | $Na_2C_2O_4$ | 32,200 | o | o M | | | o | o M | O-O | $[COO]^-$ | 0 |
| 425 | Sodium xanthate | $C_2H_5O.CS.SNa$ | v sol | o | 86 M | o | 84 J | o | 86 J | O-C | COC, S'', SM | 2 |
| 426 | Succinamide | $NH_2.CO.CH_2.CH_2.CO.NH_2$ | 4,500 | | | v sl | v sl P | | | O-O | $CONH_2$ | 2 |
| 427 | Succinic acid | $COOH.CH_2.CH_2.COOH$ | 68,000 | sl | o M | o | −14 J | o | o M | O-O | COOH | 2 |
| 428 | Succinimide | [ak] | v sol | | | v sl | v sl P | | | O-O | CONH, CO | 2 |
| 429 | Sulfanilic acid | $NH_2.C_6H_4.SO_3H$ [p] + $H_2O$ | 8,900 | o | o M | o | o J | o | o M | O-O | $SO_3H$, $NH_2$ | 4 |

TABLE 3.—(*Continued*)

| No. | Reagent | Chemical Formula | Solubility in Water, Parts per Million[d] | Results of Flotation Tests[e] | | | | | | Flotation Classification[b] | Characteristic Polar Groups | Number of "Insoluble" Carbons[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Acid Pulp | | Neutral Pulp[a] | | Alkaline Pulp | | | | |
| | | | | Froth-ing | Collect-ing | Froth-ing | Collect-ing | Froth-ing | Collect-ing | | | |
| 430 | p-Sulfobenzene azo [α] naphthylamine. | $SO_3H.C_6H_4.N:N.C_{10}H_6.NH_2$ | sl | o | −10 M | | | sl | 12 M | O-O | N:N, $SO_3H$, $NH_2$ | 12 |
| 431 | Sulfonal | $(CH_3)_2C(SO_2C_2H_5)_2$ | 20,000 | g | o M | | | g | o M | F-O | $SO_2$ | 5 |
| 432 | Tannic acid | $C_{14}H_{10}O_9$[h] | 200,000, c | o | −74 M | o | o J | o | −11 M | O-D | [h] | [h] |
| 433 | Tataric acid | $COOH(CHOH)_2COOH + H_2O$ | 1,250,000 | o | o M | | | o | o M | O-O | COOH, OH | 0 |
| 434 | Terpine hydrate | [af] | 5,000 | | | ex | o P | | | F-O | OH | 8 |
| 435 | Terpineol | [ax] | i | | | ex | o P | ex | sl C | F-O | OH | 9 |
| 436 | Tetraethyl ammonium hydroxide | $(C_2H_5)_4N.OH$ | v sol | | | | | o | o C | O-O | $[R_4N]^+$, $[OH]^-$ | 0 |
| 437 | Tetraiodo eosine | [bq] | i | | | sl | −35 J | | | O-O | COO, COC, OH | 13 |
| 438 | Tetramethyl ammonium hydroxide | $(CH_3)_4N.OH$ | 2,200,000 | | | | | o | o C | O-O | $[R_4N]^+$, $[OH]^-$ | 0 |
| 439 | Tetramethyl diamino benzophenone. | $(CH_3)_2N.C_6H_4.CO.C_6H_4.N(CH_3)_2$ | i | o | o M | | | o | 30 M | O-O | N‴, CO | 14 |
| 440 | Tetramethyl diamino dimethyl methane | $[(CH_3)_2N]_2C(CH_3)_2$ | sol | | | o | o P | | | O-O | N‴ | 4 |
| 441 | Tetramethyl thiuram disulfide. | $(CH_3)_2N.CS.S_2.CS.N(CH_3)_2$ | i | | | | | o | o C | O-O | CSNR | 4 |
| 442 | Tetrapropyl ammonium hydroxide | $(C_3H_7)_4N.OH$ | v sol | | | | | o | v sl C | O-O | $[R_4N]^+$, $[OH]^-$ | 0 |
| 443 | Theobromine | [am] | 300 | o | −9 M | | | o | −13 M | O-O | CONH, N‴ | 3 |
| 444 | Thialdin | $(CH_3.CH.NH.CH.CH_3):S_2:CH.CH_3$ | sl | | | v sl | f P | f | 92 C | O-C | NH, S″ | 4 |
| 445 | Thioanilin | $(C_6H_4.NH_2)_2S$ | v sl | | | v sl | f P | f | f C | F-C | $NH_2$, S″ | 8 |
| 446 | Thiobenzamide | $C_6H_5.CS.NH_2$ | sl | | | | | o | 40 C | O-C | $CSNH_2$ | 6 |
| 447 | Thiocarbanilid | $C_6H_5.NH.CS.NH.C_6H_5$ | i | | | o | ex P | o | 92 M | O-C | CSNH, SH, S″, NH | 9 |
| 448 | Thiocresol | $CH_3.C_6H_4.SH$ | v sl | | | | | o | 90 C | O-C | SH | 6 |
| 449 | Thiodiphenylamine | [an] | v sl | | | | | o | o C | O-O | NH, S″ | 10 |
| 450 | Thioglycollic acid | $SH.CH_2.COOH$ | sol | | | | | o | o C | O-O | SH, COOH | 0 |
| 451 | Thio [β] naphthol | $C_{10}H_7.SH$ | sl | | | | | o | 40 C | O-C | SH | 9 |
| 452 | Thiophenol | $C_6H_5.SH$ | i | | | o | g P | o | 50 C | O-C | SH | 5 |
| 453 | Thiourea | $NH_2.SC.NH_2$ | 90,000 | | | o | −65 J | o | −75 C | O-D | $CSNH_2$, $NH_2$, SH | 0 |
| 454 | Thiuram disulfide | $NH_2.CS.S_2.CS.NH_2$ | v sl | | | v sl | f P | o | 35 C | O-C | CSNH, S″ | 0 |
| 455 | Thymol | $CH_3.C_6H_3(OH)C_3H_7$ | 830 | g | o M | g | f P | g | 30 M | F-O | OH | 9 |
| 456 | Toluene azoresorcinol | $CH_3.C_6H_4.N:N.C_6H_3(OH)_2$ | sl | | | f | f P | g | 33 C | F-C | N:N, OH | 9 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 457 | Toluene sulfochloride | $CH_3.C_6H_4.SO_2.Cl$ | d | o | 10 M | | | o | −10 M | O-O | $SO_2$, Cl | 6 |
| 458 | p-Toluene sulfonic acid | $CH_3.C_6H_4.SO_3H + 4H_2O$ | v sol | | | f | 26 J | | | F-O | $SO_3H$ | 6 |
| 459 | Toluidin [o] | $CH_3.C_6H_4.NH_2$ | sl | | | f | f P | f | o C | F-C | $NH_2$ | 6 |
| 460 | Toluidin [p] | $CH_3.C_6H_4.NH_2$ | 7,400 | f | o M | g | g P | g | 26 M | F-C | $NH_2$ | 6 |
| 461 | Toluidin hydrochloride [o] | $CH_3.C_6H_4.NH_2.HCl$ | sol | | | f | 68 J | | | F-C | $NH_2$, $[Cl]^-$ | 6 |
| 462 | Toluidin hydrochloride [p] | $CH_3.C_6H_4.NH_2.HCl$ | sol | | | f | 75 J | | | F-C | $NH_2$, $[Cl]^-$ | 6 |
| 463 | Toluidin sulfate [p] | $CH_3.C_6H_4.H_2N.H_2SO_4$ | sol | | | f | 59 M | | | F-C | $NH_2$, $[SO_4]^-$ | 6 |
| 464 | Toluylene diamine [m] | $CH_3.C_6H_3(NH_2)_2$ | sol | | | o | v sl P | | | O-O | $NH_2$ | 5 |
| 465 | Tolyl hydrazine [p] | $CH_3.C_6H_4.NH.NH_2$ | sl | | | f | g P | | | F-C | NH, $NH_2$ | 6 |
| 466 | Trichlor acetic acid | $CCl_3.COOH$ | v sol | o | o M | v sl | o J | o | o M | O-O | COOH | 0 |
| 467 | Trichlor benzene (1, 3, 5) | $C_6H_3.Cl_3$ | i | o | 66 M | | | | | O-C | None | 6 |
| 468 | Trichlor phenol | $HO.C_6H_2.Cl_3$ | 800 | | | o | o J | | | O-O | OH, Cl | 2 |
| 469 | Tricrotonylene amine | $[CH_3.C:C.CH_2]_3N$ | sl | | | f | f P | | | F-C | N''' | 11 |
| 470 | Triethyl amine | $(C_2H_5)_3N$ | v sol | | | v sl | v sl P | | | O-O | N''' | 5 |
| 471 | Trinitrocresol | $(NO_2)_3.C_6H.CH_3.OH$ | 2,200 | | | v sl | v sl P | | | O-O | OH, $NO_2$ | 3 |
| 472 | Trinitrotoluene | $CH_3.C_6H_2.(NO_2)_3$ | 200 | | | o | 70 J | | | O-C | $NO_2$ | 6 |
| 473 | Trioxymethylene | ss | i | | | v sl | o P | | | O-O | COC | 0 |
| 474 | Triphenyl arsine | $As(C_6H_5)_3$ | | | | | | o | o C | O-O | As''' | 17 |
| 475 | Triphenyl carbinol | $(C_6H_5)_3C.OH$ | sl | o | o M | | | o | o M | O-O | OH | 18 |
| 476 | Triphenyl chlormethane | $(C_6H_5)_3CCl$ | i | o | o M | | | o | o M | O-O | Cl | 18 |
| 477 | Triphenyl guanidine | $C_6H_5.N:C(NH.C_6H_5)_2$ | v sl | f | o M | v sl | v sl P | sl | 86 M | O-C | NH, N''' | 15 |
| 478 | Triphenyl methane | $(C_6H_5)_3CH$ | i | o | o M | v sl | v sl P | o | o M | O-O | None | 19 |
| 479 | Triphenyl phosphine | $(C_6H_5)_3P$ | i | | | | | o | o C | O-O | P''' | 17 |
| 480 | Trithioacetaldehyde | $(CH_3.CHS)_3$ | i | | | f | ex P | | | F-C | S'' | 3 |
| 481 | Trithio acetone | $(CH_3.CS)_3$ | v sl | | | sl | f P | | | O-C | S' | 6 |
| 482 | Urea | $NH_2.CO.NH_2$ | v sol | | | o | o J | | | O-O | $CONH_2$, $NH_2$ | 0 |
| 483 | Urethane | $NH_2.COO.C_2H_5$ | v sol | o | o M | g | 25 J | o | o M | F-O | $CONH_2$, COC | 2 |
| 484 | Uric acid | ae | 600 | o | −24 M | o | −44 J | o | −62 M | O-D | CONH, NH | 1 |
| 485 | Vanillin | $CH_3O.C_6H_3(OH)CHO$-(3, 4, 1) | 10,000 | g | o M | g | o J | o | o M | F-O | OH, CO | 5 |
| 486 | Xanthic acid | $C_2H_5O.CS.SH$ | i | | | | | o | ex C | O-C | SH, S'', COC | 2 |
| 487 | Xanthogenate acetic acid | $C_2H_5O.CS.S.CH_2.$-COOH | sl | | | | | sl | o C | O-O | COC, S'', SR, COOH | 3 |
| 488 | Xanthogenate propionic acid | $C_2H_5O.CS.S.CH$-$(CH_3)$ COOH | sl | | | | | sl | o C | O-O | COC, S'', SR, COOH | 4 |
| 489 | Xylene azo [β] naphthol | $(CH_3)_2C_6H_3.N:N.$-$C_{10}H_6.OH$ | i | | | v sl | sl P | | | O-O | N:N, OH | 15 |
| 490 | Xylenol | $(CH_3)_2C_6H_3.OH$ | sl | | | g | sl P | | | F-O | OH | 7 |
| 491 | Xylidin | $(CH_3)_2C_6H_3.NH_2$ | v sl | | | g | f P | | | F-C | $NH_2$ | 7 |
| 492 | Xylyl [β] hydroxylamine | $(CH_3)_2C_6H_3.NH.OH$ | v sl | | | f | g P | | | F-C | NH, OH | 7 |

## Notes to Table 3

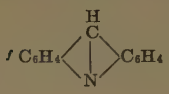
[a] Not necessarily with $p_H = 7.0$. This designation means nothing more than that no reagent of acid or alkaline nature was added.

[b] F = frothing. C = Collecting. O, in first position means nonfrothing; in second position, noncollecting. D = depressing.

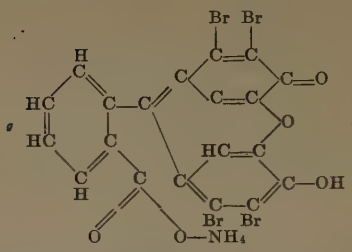
[c] "Insoluble" carbons, as here rated, are those which have no solubilizing or polar group attached to them.

[d] i = insoluble; ∞ = miscible in all proportions; v sol = very soluble; sol = soluble; v sl = very slight; c = colloidal; h = hot; d = decompose.

[e] o = non-; sl = slight; f = fair; g = good; d = decomposes; v sl = very slight; ex = excellent. M = Morrow, Anaconda Copper ore. P = Perkins, Utah Copper ore. J = Janney, Utah Copper ore. Columbia.

[f] 

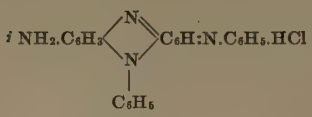
Acridine

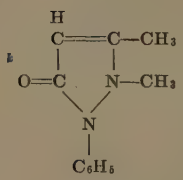
[g] 

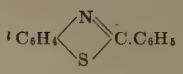
Ammonium eosine

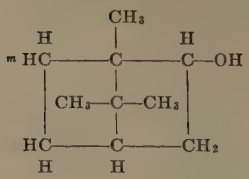
[h] Structural formula unknown.

[i] It is possible that C=C acts as a solubilizing group here, but more probable that the sample was contaminated.

[j] 

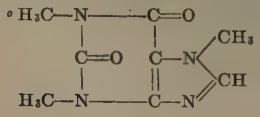

[k] 


[l] 


[m] 

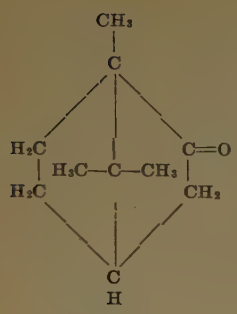
Borneol

[n] Halogens on benzene ring, unless affected by particular other substituents on the ring, produce little or no change in the hydrocarbon properties of the ring. For this reason the bromine in this compound is not considered a polar group.

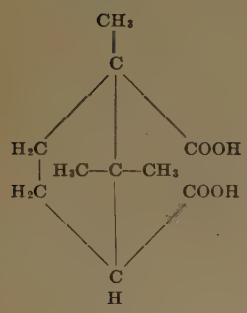
[o] 

Caffeine

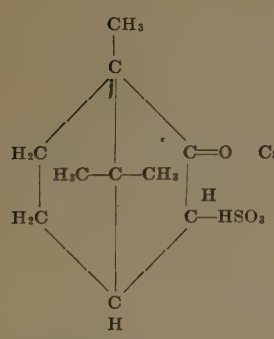
[p] Benzoic acid probably formed.




Camphor

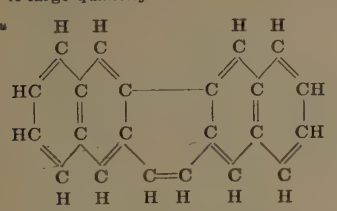



Camphoric acid

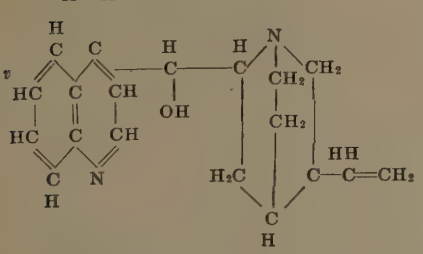



Camphorsulfonic acid

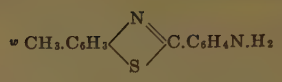
A large quantity



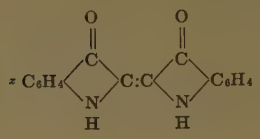
Chroysene



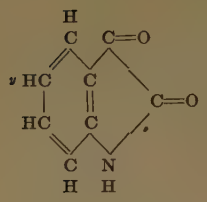
Cinchonine

w 

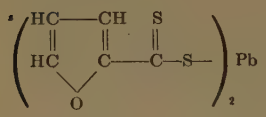
Dehydro thio [p] toluidin

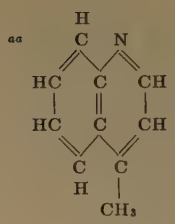
x 

Indigotin

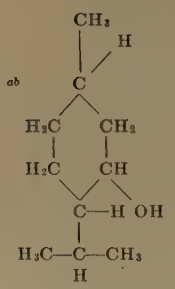
y 

Isatin

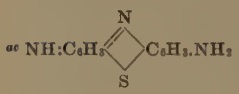
z 


aa 

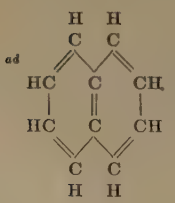
Lepidine

ab 

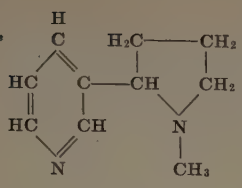
Menthol

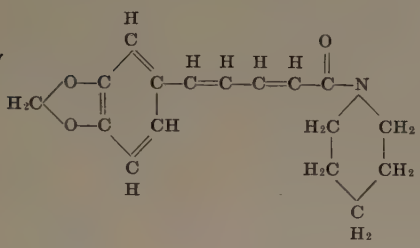
ac 

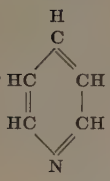
Methylene blue

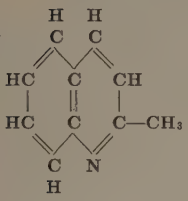
ad 

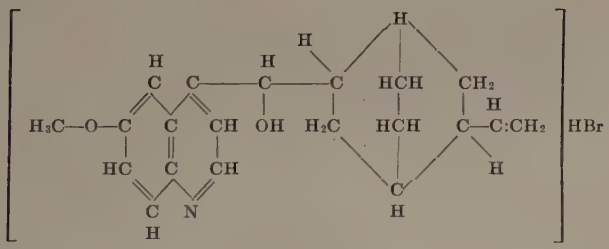
Naphthalene

ae  Nicotine

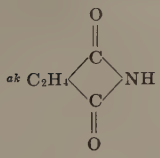
af  Piperine

ag  Pyridine

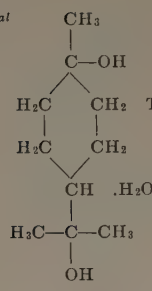
ah  Quinaldine

 Quinine hydrobromide

ai Acts in water like a simple mixture of quinoline and salicylic acid.

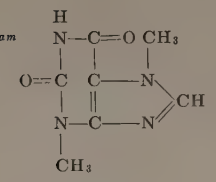
ak  Succinimide

al



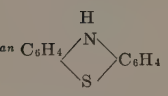
Terpine hydrate

am

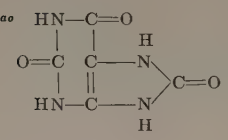


Theobromine

an

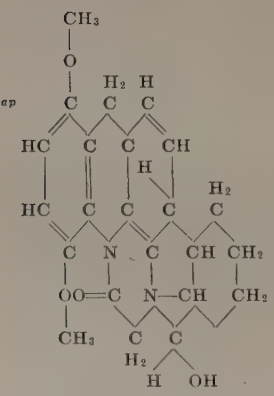


ao



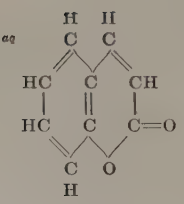
Uric acid

ap



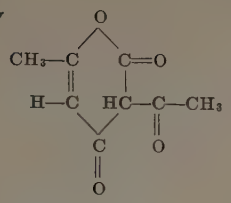
Brucine

aq



Coumarin

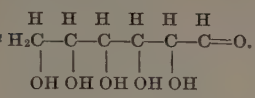
*ar*



Dehydacet carboxylic acid

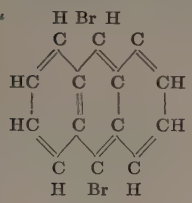
*as* Structure doubtful.

*at*



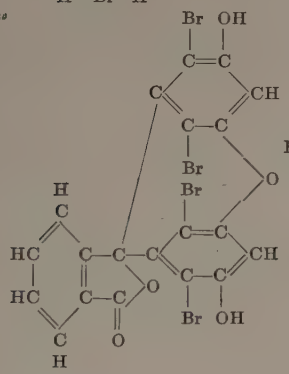
Generalized formula for 6-carbon sugars. The groups are the same in all but the geometrical arrangement differs with the different members.

*au*



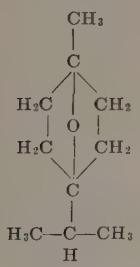
Dibrom anthracene

*av*



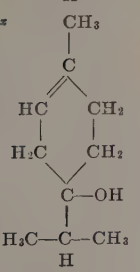
Eosine

*aw* A mixture of several substances, principally terpineal (*ax*) and cineal (below).



Cineol

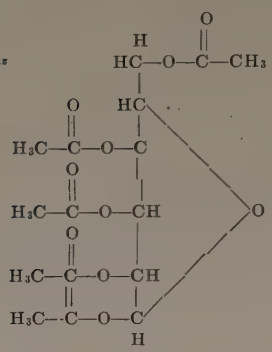
*ax*



Terpineol

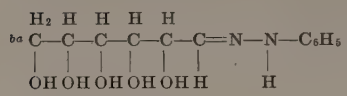
*ay* Same as *av* except that H replaces Br in all four places.

*az*



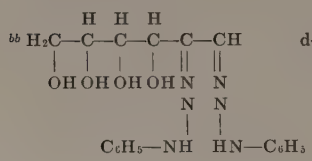
Generalized formula for the pentacetate of any aldehexose. The differences between the various specific formulas are those only that represent stereo-isomerism.

*ba*



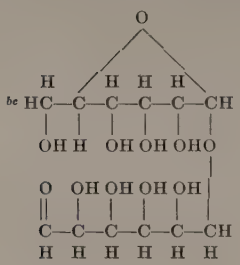
Glucose phenyl hydrazone

*bb*



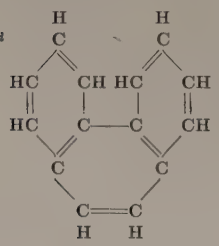
d-Glucosazone

*bc*



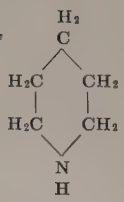
Lactose, maltose. Generalized structurla formula disregarding stereo-configuration.

*bd*



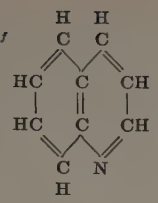
Phenanthrene

*be*



Piperidine

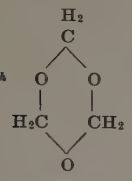
*bf*



Quinoline

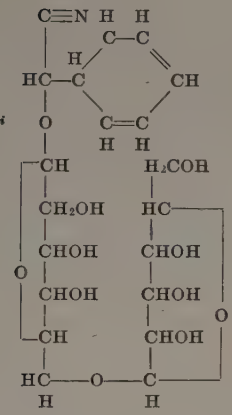
*bg* Like eosine (see note *av*) except iodine replaces bromine.

*bh*



Trioxymethylene

*bi*



Amygdalin

*bj* Like *bi* except that C:N group is replaced by COOH.

## DISCUSSION

R. E. Head, Salt Lake City, Utah (written discussion).—I am much interested in the discussion on visible Coatings. (p. 320.) There can be little doubt that the technique and manipulation employed in doing work of the character described should be developed to as high a degree of perfection as can be attained and that due precautions must be taken to insure against contamination and consequent misinterpretation of the results obtained. The work of these later investigations of the effects of cyanide and zinc sulfate on the surface of sphalerite and pyrite lead the authors to conclude that the surface effects on these minerals as pictured in the Tucker and Head paper [19] in Figs. 15 and 16 might be accounted for in part "though probably not all" by the presence of old dust deposits, rock dust, or other extraneous substances. They suggest that such contaminating substances would be removed from the portion of the surface that had been protected by the paraffin or collodion, leaving a perfectly reflective surface in contrast to that exposed to solution contact in the cell.

I recently performed a short series of experiments at Salt Lake to ascertain to what extent the pioneering work done in this field as described in the paper

[19] E. L. Tucker and R. E. Head: Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals. *Trans.* A. I. M. E. (1925) **73,** 354.

mentioned above could be verified under conditions of more refined technique. The miniature flotation cell [20] developed at Salt Lake and used in the original experiments was again used, as well as a cell developed later, built of celluloid. The impellers and shaft were cleaned with emery cloth followed by washing with ether. Adequate precautions were taken to prevent contamination from machine grease. The mineral particles used in the tests were broken from hand specimens of sphalerite and pyrite, handled only with forceps cleaned in ether and attached to the shaft between the blades of the upper impeller by means of a rubber band that had been cleaned in ether. The particles were examined microscopically before being attached to the shaft, to be certain that they had no visible dust coatings, grease or tarnish contaminations. In some instances, microscopic sulfide particles were removed by means of a clean rubber-tipped glass rod.

Neither collodion nor paraffin was used to coat the particles. The use of paraffin is open to the objections noted by Messrs. Taggart, Taylor and Ince, but it is of more than passing interest that collodion cannot be satisfactorily used in Salt Lake. A lengthy discussion of this fact is not warranted here, but it may be stated that in the brief time required to transfer the collodion from the container to the particle surface, a coating appears to form on the collodion drop, which prevents tenacious adherence to the mineral surface, and during the ensuing evaporation and treatment in the cell it shows a marked tendency to peel. In some cases the collodion has come off altogether in the cell and in no instance has it adhered sufficiently to prevent the cell solution from penetrating between it and the mineral surface.

A cleaned metal "pointer" was used to flex the band sufficiently to permit the mineral particles to be placed in position, with forceps, under the rubber band around the upper impeller. Tests were run for a period of 20 min., using NaCN and $ZnSO_4$ in the proportions of 2 lb. NaCN to 4 lb. $ZnSO_4$[21] per ton. The cyanide and zinc sulfate were combined in a clean beaker and sufficient distilled water was then added to fill the cell to capacity. The solution was immediately transferred to the cell and the agitation continued for 20 minutes.

At the conclusion of the test, the particles were removed from the cell in the same manner as they were introduced and were washed successively in three beakers of distilled water and then dried before a 14-in. fan operating at high speed. They were then examined microscopically and photographed (Figs. 47 and 48). It is interesting to note that the surface effects differ somewhat on the respective minerals; the particles on the sphalerite show a distinct tendency towards crystallization and are apparently rhombohedral, while those on the surface of the pyrite do not exhibit this phenomenon.

The writer is not justified in attempting to discuss this phase of the subject in detail at the present time, except to state that microscopic examination of the cell solution shows the presence of crystals similar in form to those shown on the sphalerite surface. The maximum size of the particles in the NaCN-$ZnSO_4$ solution examined was 5 microns. Particles of about 0.5 micron size were also distinguishable, but whether they are crystalline in form has not yet been determined. Further investigation along this line may result in information on the subject, although there is a limit to the visual range of the microscope.

The difference in the machine used at Salt Lake and that used in the experiments made at Columbia may account, at least in part, for the difference in the surface effects produced on sphalerite and pyrite.

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[20] J. F. Gates and L. K. Jacobsen: Flotation Fundamentals and Their Application. Univ. of Utah, Dept. of Metallurgical Research, *Bull.* 16 (1925).

[21] The fact that zinc sulfate is hydrous, as shown by the formula $ZnSO_4 . 7H_2O$, must be borne in mind in properly proportioning the reagents.

The experiments of Messrs. Taggart, Taylor and Ince on the subject of slime coating are of particular value and interest, although "Anaconda slime" is a term of somewhat indefinite or broad meaning in so far as conveying a definite idea of its chemical and mineralogical composition. Under the conditions of performing the experiments, decanting the slime portion of the ore for the cell experiments would obviously involve working with a pulp containing a concentration of the soluble constituents. The general character of "Anaconda" slime, as well as its physical and chemical composition, is dependent largely on the character of the original ore, and changes due to oxidation, contamination, etc.

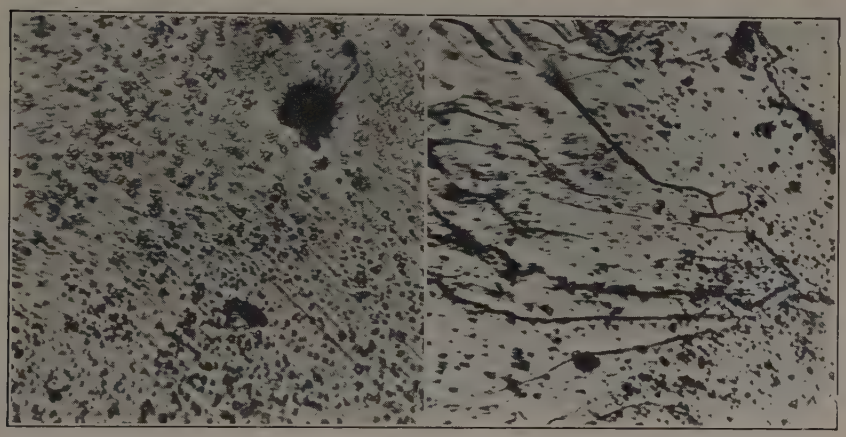

FIG. 47.—PYRITE AFTER TREATMENT.
FIG. 48.—SPHALERITE AFTER TREATMENT.

Previously clean surfaces after treatment for 20 min. in a 50-gram miniature flotation cell with NaCN and $ZnSO_4$ in the proportion of 2 lb. NaCN to 4 lb. $ZnSO_4$ per ton of ore.

In Fig. 48 note the symmetrical form of the particles adhering to the surface and the fact that they are different from those shown in the photomicrograph of the pyrite surface.

Both taken at a magnification of 600 × with conical stop illumination. [See H. S. George: Simulating Natural Light in Metallography. *Trans.* A. I. M. E. (1924) **70**, 259–273.]

A. E. ANDERSON, Salt Lake City, Utah (written discussion).—The authors have presented an excellent paper and have introduced to the profession many ideas regarding the functions of reagents in flotation. The chemical reactions of collecting agents with oxidized minerals forming insoluble coatings, as discussed in this paper, have been encountered by Gaudin and Martin[22] and also more recently. The formation of these insoluble coatings upon the mineral surface is one of the primary functions of the collecting agents and the authors' discussion of this function is both interesting and important.

On page 303 the authors say, "A crystal of cerussite, (natural lead carbonate), soaked in a solution of thiocresol, becomes covered with a yellow coating of lead thiocresylate, but is not rendered readily attachable to bubbles." My observation

[22] A. M. Gaudin and J. S. Martin: Flotation Fundamentals, III. Utah Eng. Expt. Sta. *Tech. Paper* 5, Figs. 7A and 7B.

confirms the rapid formation of canary yellow lead thiocresylate on cerussite crystals. However, on the basis of the authors' valuation of bubble-machine test results, as criteria of floatability, the statement that a lead thiocresylate-coated cerussite particle is not readily attachable to bubbles would naturally be construed to mean that it will not float. Our experiments, run in a 50-g. all celluloid agitation machine, of the University of Utah type, which are of course a direct measure of floatability, indicate that lead-thiocresylate-coated cerussite floats readily. This is shown by Table 4 and Fig. 49.

TABLE 4*

| Reagents | | | | Tailing Solution | | Concentrate | | | Tailing | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Terpineol, Lb. per Ton | p. Thiocresol Lb. per Ton | Preagitation, Minutes | Float, Minutes | pH | Temperature, Deg. C. | Weight, Grams | Assay Pb, Per Cent. | Rec., Per Cent. | Weight, Grams | Assay Pb, Per Cent. | Loss, Per Cent. | |
| 0.20 | | 2 | 6 | 7.8 | 18.0 | 4.6 | 26.5 | 15.8 | 44.8 | | | Pulp for assay of tails lost. |
| 0.20 | | 2 | 6 | 7.8 | 20.0 | 5.2 | 23.3 | 15.7 | 43.0 | 14.6 | 81.0 | |
| 0.20 | 0.125 | 2 | 6 | 8.0 | 20.0 | 8.2 | 51.5 | 54.6 | 41.0 | 8.1 | 43.0 | |
| 0.20 | 0.125 | 2 | 6 | 8.0 | 18.0 | 8.3 | 52.1 | 56.0 | 41.0 | 8.3 | 44.0 | |
| 0.20 | 0.25 | 2 | 6 | 8.0 | 18.0 | 9.8 | 66.4 | 84.0 | 39.6 | 3.3 | 16.9 | |
| 0.20 | 0.25 | 2 | 6 | 8.0 | 18.0 | 9.8 | 64.4 | 81.5 | 39.7 | 3.4 | 17.4 | |
| 0.20 | 0.50 | 2 | 6 | 8.0 | 18.0 | 11.3 | 66.8 | 97.8 | 37.9 | 0.25 | 1.2 | |
| 0.20 | 0.50 | 2 | 6 | 8.0 | 18.0 | 11.6 | 64.7 | 97.0 | 37.7 | 0.23 | 1.1 | |
| 0.20 | 1.00 | 2 | 4 | 8.0 | 21.0 | 11.4 | 67.0 | 99.0 | 38.5 | 0.25 | 1.2 | |
| 0.20 | 1.00 | 2 | 4 | 8.0 | 20.0 | 11.7 | 65.6 | 99.5 | 37.7 | 0.11 | 0.5 | |
| 0.20 | 2.00 | 2 | 4 | 8.0 | 20.5 | 13.8 | 58.1 | 99.5 | 36.0 | 0.06 | 0.3 | |
| 0.20 | 2.00 | 2 | 4 | 7.8 | 20.0 | 12.9 | 59.0 | 100.1 | 36.7 | 0.06 | 0.3 | |
| 0.20 | 3.00 | 2 | 4 | 7.8 | 21.0 | 13.3 | 58.0 | 100.0 | 36.5 | 0.06 | 0.3 | |

* 10/40 mixtures of deslimed cerussite and calcite used throughout; both minerals −100 mesh, and desliming conducted so as to remove substantially all −800 mesh material. The calcite was 99 per cent. + $CaCO^3$ and the cerussite was a crystalline, extra pure, containing 99.5 + $PbCO^3$.

A. M. GAUDIN, Butte, Mont. (written discussion).—This comprehensive study of the functions of flotation reagents constitutes one of major contributions to the literature of flotation and has been of the highest interest to me. It is, no doubt, due to the great length of this paper that the authors have chosen not to include a detailed description of the analytical methods employed by them to determine the contents of collector solutions, such as thiocarbanilid and thiocresol solutions. The content of these reagents may, perhaps, be determined by the same method that is used to determine xanthate, which consists in oxidizing these reagents with iodine, as indicated by the following reaction:

$$2ROCSSK + I_2 \rightarrow (ROCSS)_2 + 2I^- + 2K^+$$

This reaction is very sensitive (starch being used as an inside indicator). It is dependable to determine 1 part of xanthate in 100,000 of solution, and with careful manipulation can be made more sensitive.

The "captive-bubble test" described by the authors is a most ingenious contrivance making use of the old "contact angle" idea in an elaborate manner. Although the method is graphic, and, unquestionably, a rough criterion of floatability, its weakness lies in that it is an indirect method to quantify something which can be quantified directly, and in that the measure of collection it yields is based on the floatability of

one or two mineral particles, which on account of surface alteration may not be representative of that mineral. Flotation tests conducted in miniature flotation cells depend upon the performance of millions of grains at a time rather than upon that of a single grain. They stand, therefore, a good chance of being more representative. The fact that the captive-bubble test cannot be depended upon to give more than qualitative data is exemplified, for instance, in a comparison of the collecting ability of amyl xanthate and of that of ethyl xanthate. Laboratory tests with miniature flotation cells, large-scale tests and plant runs substantiate the fact that amyl xanthate is a better collector than ethyl xanthate; the captive-bubble test shows the contrary (Table 1). Comparisons of the performance of amyl disulfide and amyl mercaptan; ditolyl thiourea and diphenyl thiourea; dixanthogen and xanthate vs. mercaptan and disulfides; heptyl mercaptan and amyl mercaptan; thiocresol and amyl mercaptan, all indicate that the captive-bubble test is at variance with the results obtained with pure minerals and with ores in testing cells.

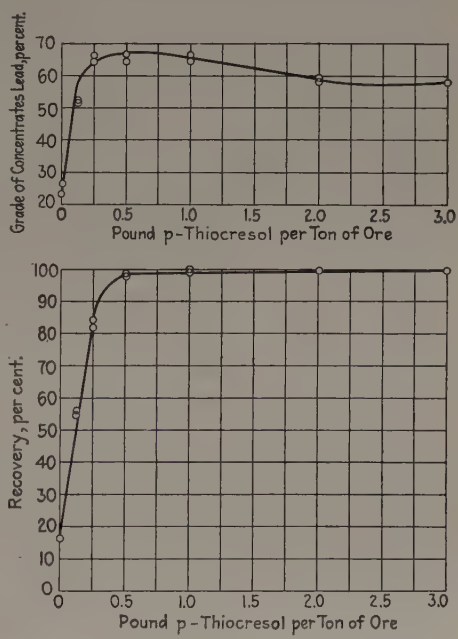


FIG. 49.—RECOVERY OF CERUSSITE COATED WITH LEAD-THIOCRESYLATE.

The authors advance and develop the view that collecting agents proceed by double decomposition with oxidation products occurring at the surface of the sulfide minerals. The same view was arrived at, independently, by Kellogg Krebs who writes[23] that "essentially flotation is an oxidation process followed by chemical precipitation," and also that, upon addition of xanthate or dicresyl dithiophosphates, "the film of cupric hydroxide formed upon the oxidized surfaces of copper sulfides is altered to the cupric xanthate or cupric dicresyl-phosphate." The fact that collecting agents of the xanthate or hydrosulfide type collect copper carbonates as the result of double decomposition has been demonstrated.[24] The same is true of lead carbonates.

The authors refer to collector and frother molecules as consisting of two portions, one of which is "water-avid" and the other "water-repellent." There is no question as to the wise choice of these terms, which are self-descriptive. However, in the interest of the readers, it should be mentioned that the meaning of these terms, as construed by the authors, is identically the same as that of the terms "polar" and "nonpolar," respectively, which have been used before.[25] Furthermore, the discription of water-avidity and of water-repellency in terms of polarity and nonpolarity is in agreement with accepted chemical terminology, as indicated by the use of these

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[23] Private communication, August, 1928.

[24] A. M. Gaudin and J. S. Martin. *Op. cit.*

[25] A. M. Gaudin: Flotation Mechanism, a Discussion of the Functions of Flotation Reagents. Flotation Practice, A. I. M. E. (1928) 50–77.

terms by such eminent authorities as Langmuir, Harkins, McBain, Freundlich, Bancroft and others.

The authors take exception to the conclusions of Tucker and Head[26] as to the coating of sulfides by treatment with lime, cyanide and zinc sulfate. Without going into the details of the procedures employed, it would not seem out of place to consider the relation between the Tucker and Head tests and the authors' tests with practice. In the original experiments performed by Tucker and Head, and in the new experiments by the authors the ratio of quantity of reagent to mineral surface is enormously greater than it is in practice. Recent work by Gross and Zimmerley at the Intermountain Station of the U. S. Bureau of Mines has shown that the average size of sphalerite grains in samples of flotation pulps taken from various mills is in the vicinity of 10 microns. If the sphalerite content of the average ore milled by selective flotation is placed at 10 per cent., the sphalerite area per gram of ore is but one-tenth of the total area of the ore. The area of the ore per cubic centimeter is approximately 9000 sq. cm. (allowing for the shape of the particles), so that the sphalerite area per gram of ore is substantially 225 sq. cm. In other words, a 50-g. charge of ore would contain about 11,000 sq. cm. of sphalerite surface, if it conformed to the conditions of practice, in place of the few square centimeters represented by one spall of mineral as used by Tucker and Head or by the authors. The density of the coatings on the new pictures obtained by Mr. Head is such that not over one-tenth of the surface is visibly coated by a discontinuous film. Furthermore, Mr. Head's results were obtained through the use of 2.0 lb. of cyanide per ton of ore (if the ore were present in the cell). This amount is about five times as large as is used in practice. In other words, the pictures shown by Mr. Head were taken under conditions representing an exaggeration of the cyanide and zinc sulfate concentration, as compared with the surface of the mineral, of some 10,000 times over the conditions used in practice. It is, therefore, hard to believe that the considerably more tenuous visible films that might result under the conditions of practice would have any substantial effect on the flotation of sphalerite.

Mr. Ince has shown[27] that alkali cyanide and zinc sulfate do not affect the state of dispersion or of flocculation of slime. It would therefore appear that the function of cyanides and of zinc sulfate is neither to produce material, visible coatings nor to affect slime dispersion. Work at the University of Utah,[28] which is nearing completion shows that the action of these two reagents is entirely chemical (adsorption being construed to be a chemical phenomenon).

W. M. Grosvenor, New York, N. Y. (written discussion).—It is difficult to avoid being carried away by enthusiasm over the interesting and valuable work and the clear compact way in which the authors have presented so much of what has been done by themselves and others in ascertaining the forces at work in modern air-froth flotation. They deserve such hearty commendation that one shrinks from offering even a word of what may seem like criticism.

Regardless of enthusiastic appreciation, however, such a valuable assemblage of information requires criticism just because its general usefulness makes it more than ordinarily dangerous to students and young engineers in the field should it by accident present any misinformation, unwarranted assumption, or omission of some essential factor.

Many readers may not have Professor Taggart's familiarity with the large amount of scientific study given to the main underlying principles of flotation. Therefore it

[26] E. L. Tucker and R. E. Head: *Op. cit.*

[27] See page 261.

[28] A. M. Gaudin, E. C. Haas and C. B. Haynes: Flotation Fundamentals, IV. Utah Eng. Expt. Sta. *Tech. Pub.* 8.

seems wise to amplify some statements that might be misunderstood, to supply some important omissions and to correct one or two errors of fact.

The "Summary, etc." on page 258 is likely to be misunderstood. After the statement that "U. S. Patent 835120 issued in 1906 to Sulman, Picard and Ballot" was "*the first practicable*, foolproof method of froth flotation" we find the apparent contradiction that "A number of less simple methods of producing *the same result* had been described previously in patent publications and otherwise." If the modern flotation process were described as *air-froth* flotation, the other apparently contradictory statement would have been unnecessary, because none of the prior processes in fact did produce that result.

The "frothing agent" and the "oiling agent" were clearly recognized as distinct in 1909 when the second or "soluble agent" patent was applied for. The former acts chiefly at the water-air interface to "modify" the air-water surface tension, promote "aeration" and prevent "dropping" of the mineral. The latter, in minute quantities only, acts by "smoothing" the rougher ore particles, by filling irregular hollows and by increasing the "nonwetting" quality of the mineral surface, thereby promoting more ready attachment of air to mineral, and is called a "collecting" agent by these authors.

Absence of strong aeration or of a frothing agent does not *prevent* the strongest attachment of air bubbles to mineral or metallic particles, but no useful froth will be formed. Something is required to make the air subdivisible into small bubbles

Fig. 50.

Fig. 51.

Fig. 52.

and to retard their violent coalescence, which causes dropping of mineral. This was clearly shown at the Miami trial when the violence of coalescence in unmodified water was illustrated and the calculation of the time of coalescence (1/12,000 sec.) was explained. The frothing agent may be a practically insoluble "oil," like oleic acid, which not only spreads over the air-water interface but is able to produce self-adjusting variations in the surface tension thereof. The frothing agent may also be a substance dissolved in the water and adapted to produce self-adjusting variations in the surface tension, perhaps by positive or negative absorption.

The presence of too much oil (whether of such frothing oil or of a nonfrothing oil like purified petroleum oil) produces a sort of bulk-oil flotation, more or less assisted by air bubbles caught in the oil. Such oil excess, however, destroys the direct strong attachment of air bubbles to mineral, making an oil froth. Hence, in flotation practice, overoiling leads not only to waste of oil but also to lower recoveries, as was clearly shown by the company's own records in the Butte & Superior case. This results from a complete change in the method of attachment of the air bubble to the mineral.

So it is not correct to state (p. 286) that the patent "was sustained in the U. S. Supreme Court largely on the basis of an erroneous theory that the physical phenomena involved passed through a critical point as the quantity of oil was reduced," that the patent "specified 1 per cent. by weight on the ore as the upper limit of operable oil quantity," and that "it was not until after many years of practice that the quantity of oil generally used got down to between 1 and 2 lb. per ton of ore." In fact, all three statements are practically incorrect

In the first place, with decreasing proportions below 6 or 8 per cent. by weight of oil on the mineral, there is for each oil and each mineral particle a critical change in the physical phenomena controlling the strength of attachment of that particle to the air bubble. The location in percentage of this point of critical change depends on the relative thickness of the oil layer on the surface of the mineral, on the oil-water surface tension, viscosity, etc. for the particular oil involved, and probably also on the character of the mineral. This was thoroughly illustrated by moving pictures of the captive bubbles and particles of galena and metal in two of the trials. The forces were calculated and the critical thickness of oil layer calculated and demonstrated for a specific ore with oleic acid (the preferred oil of the patent) and other oils. In a simple practical way, we may say that if a small, clean, bright galena particle or an aluminum disk is carefully scrubbed with soap and water, washed and rinsed by overflow of excess distilled water, it practically hangs suspended *in* the bottom of the air bubble (Fig. 50). The surface tension lift of the clean air-water interface is about 76 dynes per cm. of peripheral length of the line of contact in Fig. 50. If a minute amount of oleic acid is added, about sufficient to form a coating 1/100,000 in. thick on the mineral particle, it settles into the position shown in Fig. 51. The more or less modified surface tension of the air-oil (30 dynes) plus oil-water surfaces (15 dynes) in Fig. 51 is about 45 dynes per cm. of periphery at the line of contact. When the amount of oleic acid is increased enough to form a layer more than about 1/30,000 in. thick on the particle it sinks into the position shown in Fig. 52. Here the only surface tension capable of supporting the mineral particle is the oil-water interfacial tension of about 15 dynes per cm. If the particle is a cube of galena weighing much more than 5 to 15 mg. according to the kind of oil, it will pull out an elongated thinning neck of oil and fall off (even from a stationary bubble) whereas in Fig. 50 a 45-mg. clean cube of galena can be lifted. Similarly, in Fig. 11, it is clear that only in the exceptional case (if there be any such) in which the oil-water interfacial tension is as great as that of the air-water interface, can we hope to get the full pulling power and elongation of the bubble.

It is therefore incorrect to speak of the courts being misled "largely on the basis of an erroneous theory that the physical phenomena involved passed through a critical point . . . " They certainly do.

Equally incorrect is the statement that the patent, "specified 1 per cent. by weight on the ore as its upper limit of operable oil quantity." The patent recommended "a very small proportion of oleic acid (say from 0.02 per cent. to 0.5 per cent. on the weight of the ore)." Certain claims (9, 10, 11) were limited only to "a small quantity of oil" whereas others were more limited to "a fraction of one per cent." The court held the first group invalid *because indefinite* in the Hyde case (242 U. S. 261) and reaffirmed *its* limitation to "a fraction of one per cent." in the Butte & Superior case (250 U. S. 336), largely basing its decision on its previous finding.

Again, it is incorrect to say that "it was not until after many years of practice that the quantities of oil generally used got down to between 1 and 2 lb. per ton of ore." The patent speaks for itself. The original discovery was made with 0.1 per cent. (2 lb. per ton). All of the early licenses operated on quantities of this order. Some of those held to infringe if they used less than 1 per cent. and seeking to avoid the patent, wasted oil and sacrificed recoveries by using vastly more. It is significant that they settled for $5,000,000 rather than continue the lower recoveries caused by over 1 per cent. of oil.

The statement in the middle of page 286 may also be misleading, to wit, "On its face this patent was for use as the froth-producing agent in a particular type of froth flotation; *viz.*, the agitation-froth process, of certain classes of water-soluble organic compounds . . . " To the layman this means that the process was limited in its descrip-

tion and claims to the use of a particular form of apparatus as one of the essential elements of novelty. Such was not the case. The specification says "a gas is liberated in, generated in, or effectively introduced into the mixture;" *i.e.*, the pulp. Some of the claims read specifically to "agitating the mixture and *beating* air into it" whereas others read to "agitating" but are in no way limited to beating. Few of us would deny that one of the best known and oldest methods of agitating was by air blown in under a false bottom or into the central tube of a Pachuca tank.

Again, in the next paragraph, occurs one of those unintentionally casual statements that are all too apt to cause an earnest student endless doubt and trouble; *viz.*, "The patent corporation, however, succeeded in convincing the courts of the Third Circuit that this patent covered, in addition to the soluble organic compounds specifically listed or generically indicated, the water-soluble portions of the 'oils' of Patent 835120 on the theory, good for patent litigation but of no weight scientifically, that while oils floated sulfide mineral because they coated them, these soluble mineral-frothing agents must act in some different way because, being in solution, they could not coat." This might lead the student of the paper to believe that the soluble portion of the organic compounds did not independently exercise the function of regulating the surface tension at the air-water interface (stabilizing the bubbles and thereby aiding air emulsification and avoiding violent coalescence), while the insoluble portion simultaneously exercised the independent function of increasing the ease of attaching the air bubbles to the mineral by coating the mineral surface and making it less rough and more water-repellent. Yet, as a matter of fact, throughout the paper the authors recognize both of these independent effects. This coating is repeatedly described as just what occurs and photographs are presented to illustrate it.

Incidentally, the described method of preparing particles for photographing or for determining the so-called "collecting indices," leaves the operator with no remote idea of the actual amount of oil on mineral, or ratio of flotation agent used to mineral present. Such omission would seem to vitiate most of the conclusions based on such comparisons, whether made by contact angle or by distortion ratio or by collecting index. The value of the distortion ratio, both absolute and comparative, seems to depend first on the certainty with which all *excess* oil (insoluble portion) is removed, and secondly on the amount of oil (insoluble portion) remaining, and thirdly on the amount of frothing agent (soluble or insoluble present at the bubble surface) modifying the surface tension of the bubble. The results, page 332, show that even in pure water the distortion ratio varies from 2 times the contact angle ($\times$ 100) down to $\frac{2}{3}$ the contact angle ($\times$ 100), a range of accuracy or error approximately 3 to 1, or 300 per cent. What excuse is there for averaging such wide variations and why valuate the change in distortion 100 times as much as the contact angle? The authors appear to assume that elongation measures lifting power. If this assumption is either practically correct or mathematically demonstrable, the proof is lacking. I prefer actually to weigh the pull of the bubble on the lifter (or on the particle).

In my own work we separated the mineral actually floated with known quantities of agents in the operation, determined the amounts of agents left in the treatment water, and the amounts left on the mineral, and tested and photographed the mineral while immersed in a clear portion of the treatment water. Thus we obtained photographs (at from 500 to 900 dia.) of the oil distributed on the surface of floated mineral known to carry 1.8 lb. per ton. In this way we were not left to guess how much we chanced to pick up by wiggling the particles held between tweezers for an arbitrary time of 5 min., in an emulsion of unknown stability and unknown degree of dispersion; or guess again how much had been redissolved in the fresh water used for examination of the particles.

At the top of page 290 occurs a statement which is misleading in rather important particulars. It reads: "In the trial of Minerals Separation, Ltd. *vs.* Miami Copper Co., W. M. Grosvenor performed an experiment in which bubbles, held captive in the bulb of a small thistle tube inverted under water, were used in attempts to pick up small mineral particles." It is highly important to the understanding of flotation phenomena by the student or engineer in the field that the experiments were not "*attempts* to pick up *small* particles of mineral" and were not confined to "bubbles *held* captive" in a bubble holder. The numerous particles that were shown to be actually lifted, *whenever they were clean*, were 0.88-mm. galena cubes weighing 5 mg. up to 1.75-mm. galena cubes weighing 40 mg., and aluminum punchings $\frac{5}{32}$ in. dia. and from 0.014 in. thick weighing 42 mg. up to 0.085 thick weighing 255 mg. The latter were used for more exact measurement of lifting power. Also, there was an aluminum disk about the size of a 25-cent piece lifted on a large bubble. It was shown that, while observably oiled, all but the lightest of these particles could not be lifted by air bubbles. Furthermore, that if picked up while clean, all but the lighter ones *dropped off* when about 1 per cent. of their weight of oil was applied to the side of the air bubble. Finally, the progressive removal of oil from an overoiled galena particle by successive *free-moving* air bubbles was shown. The 20-mg. particle would not lift up at all on the bubbles at rfist because the oil connection necked-off. Later, as the oil grew less and less, and became invisible, the particle became highly active, and finally clung to the bubbles and rode up to the surface again and again. These are scientifically and technically important facts which the paper by Taggart, Taylor and Ince fails to present in their proper relation to flotation phenomena.

Again I wish to congratulate the authors on their work. In fairness to them, it should be remembered that these comments do not generally involve criticism of them or their work. Most of the facts were first presented more than 10 years ago, and were merely a matter of court record, unpublished in the journals and easily overlooked. They are, however, matters of moving picture record which it would be a pleasure to present before the Institute if opportunity should arise.

E. A. Hersam, Berkeley, Calif.—In this matter of adsorption and the consumption of collecting agent or modifying agent, we all need to be appreciative of the almost infinitesimal quantity of anything necessary to be serviceable as an adsorbing agent. There is a vast difference between dealing with layers or coatings that are visible under the microscope, or that are perceptible, and coatings that are necessarily only one molecule deep to present a modified exterior of sulfide particles. So much is that true that it is better for us in the abstract to treat of adsorption as a theoretical potentiality rather than a measurable attainable value. We are dealing with a word that is a magic word in accounting for some of these phenomena, but in quantities we want to hold that down to molecular proportions.

The difference between the size of a molecule and the size of a dust particle that is as small as any dust particle that we can conceive of is an incredibly wide difference, a span between the size of a balloon and the size of a grain of wheat, and the small quantity of material necessary for providing a modified molecular surface on a sulfide particle is something almost out of our grasp. If there is consumption of chemical agent or of conditioning agent or of collecting agent, we have to look to some other place of escape and utilization than merely as a serviceable function on the surface of the sulfide or mineral particle itself. We must keep that difference between the size of a molecule and the size of a dust particle well in our minds when we deal with these questions.

A. F. Taggart.—Mr. Anderson was right in his assumption that on the heavily coated thiocresylate particles we were unable to get an indication of floatability by the

bubble machine. On the other hand, we have worked with cerussite in flotation machines, treated with thiocresylate, and there is distinct concentration. This is confirmed by the flotation of lead carbonate at Chief Consolidated, which has been recently described, using xanthate instead of thiocresylate.

The explanation is, of course, that when a thiocresylate coating is heavy enough to be seen with the naked eye, all orientation is lost and you do not get the water-turning effect of the hydrocarbon that you do when there is a substantially monomolecular film of lead thiocresylate with the sulfur end of the thiocresol molecule against the cerussite particle and the hydrocarbon end sticking out. In a flotation cell flotation takes place as soon as the first reaction layer is completed.

It is of interest to note in this connection that the high consumption of the sulfhydro type collectors that occurs when they are used to float oxidized ores may be decreased by first sulfidizing and then permitting slight oxidation of the sulfidized surface, as by agitation in air-saturated water.

I noted one inaccuracy in the reading of Mr. Head's discussion, I think, where he said that pouring off slime water gave a pulp in which the soluble salts were concentrated. It may be that that was a mistake in the writing. But, of course, when you put salts into water and shake them up and dissolve them it does not make much difference what part of the water you pour off, the concentration of the dissolved salt is the same in the part poured off as in that left behind. There is some confusion there.

Professor Gaudin raised the question of analysis. We used a modification of the iodine method. Professor Gaudin says that is accurate to 1 part in 100,000. Our work goes well beyond this. With solutions of potassium ethyl xanthate containing about 15 mg. per liter of water, duplicate analyses accord to within 1.5 to 2 per cent. of the xanthate present, which is to say, to 1 part in better than 3,000,000. We were determining extremely minute amounts of material abstracted from very dilute solutions. We often started with solutions that contained not more than one part of reagent in 100,000 parts of water, and we had to determine percentages of abstraction from such solutions with some degree of accuracy, so instead of using starch as an indicator, we used the layer method with benzol.

I was much interested in Professor Gaudin's criticism of the bubble machine as a test of floatability, and rather surprised at his conclusion that it was not as accurate as the miniature cell test that he has done so much work with. Since I have had his discussion I have worked over two or three papers that he has published directly from the University of Utah during the last year. Although the details of the investigation are not of any particular interest, they lead to the conclusion that when Professor Gaudin used the same concentrations that we did, and the same agent, he got the same comparative results. That fact is not apparent on the surface of his results, on account of contradictions, but appears when the nonconcordant elements of his work are properly weighted.

I did not get the drift of the reference to Mr. Krebs. Of course, there is nothing particularly new in the idea of double decomposition chemical reaction as the explanation of the action of these reagents on sulfide minerals. One of the authors of this paper gave that material in court room trial something over a year ago and at a lecture at the Institute in April, 1928. The lecture was published in June, 1928, in the Flotation Practice volume.

With respect to the statement that the concentrations, or, at least, the ratios of the weights of reagent to sulfide surface exposed are different in the bubble machine from what they are in the flotation cell and are, therefore, to be used with care: Some years ago, when it first occurred to us that there ought to be some relation between the amount of reagent used and the amount of mineral floated, we made parallel tests

between copper ores containing about 1 per cent. mineral and zinc ores containing about 15 per cent. mineral. With the same grinding, there was 15 times as much surface in one case as in the other. About the same minimum amount of reagent was required to produce a given amount of flotation in each case. This was confirmed by mill results. In other words, there is not any direct relation between the amount of collecting agent that is necessary to get effective flotation and the amount of mineral in the flotation machine. It would seem to be rather a question of solution strength.

The material in Dr. Grosvenor's discussion has been briefed so many times in the various cases to which he refers that to reopen the discussion here by picking up the accustomed cudgels against him would be a waste of time. As he infers, anyone sufficiently interested can find it all buried in the records of now closed cases. So much for matters of opinion.

As to facts, however: Fig. 50 is incorrect, as observation of the phenomenon will show. Furthermore, the particle would wet completely and not float, if it were not contaminated with oil or some other organic compound equivalent to oil in so far as collection is concerned.

It is interesting to note that since Dr. Grosvenor's discussion was written the U. S. Supreme Court has reversed the finding of the Third Circuit Court of Appeals that there was new matter over Patent 835120 in Patent 962678, and commented on the character of proof urged by the patent corporation in the following trenchant words:

"It is said that the oil does it [floats the mineral] by coating the metal particles and that of course a substance in solution could not do that. There is no 'of course' as to what nature can do except as proved by observation and experiment." (Bracketed material added.)

Dr. Grosvenor's troubles with our bubble-machine tests would be in part resolved by reading the description printed in the paper. That would answer his rhetorical question at least. The basis for our belief that it is the ratio of collector to liquid that is important rather than the ratio of collector to mineral surface has already been discussed.

# Reducing and Oxidizing Agents and Lime Consumption in Flotation Pulp

By Oliver C. Ralston,* Leonard Klein,* C. R. King,* T. F. Mitchell,* O. E. Young,* F. H. Miller* and L. M. Barker,* Clarkdale, Ariz.

(San Francisco Meeting, October, 1929)

Flotation is now commonly practiced in alkaline ore pulps, yet little is known regarding the action of the alkaline solutions on the ore particles beyond the fact that films of oxidized material form. We wish to chronicle our discovery of the presence of soluble reducing agents in alkaline ore pulps of the United Verde, and present some data on lime consumption.

During the grinding and flotation of a pyritic ore containing small amounts of ferrous sulfate and other soluble salts, an excess of lime was added to precipitate the salts, and filtered samples of the solution were titrated with standard permanganate solution. Even in pulps of high causticity an appreciable permanganate titration was always obtained, in spite of the fact that the solutions were shown to contain little iron. Investigation of the cause brought about the discovery of several previously unsuspected compounds in flotation pulps made from pyritic ore. Not only the reducing agents present had to be identified, but also the amount of dissolved oxygen, and a survey was finally made of the free oxygen content and reducing agents of the mill pulp in the concentrating mill at Clarkdale.

A great many compounds might form, caused by oxidation of pyrite or other metal sulfides or by reaction between a lime solution and pyrite. The most probable compounds considered were calcium sulfides, polysulfides, thiosulfates, and polythionates. Later it was discovered in the literature that in alkaline pulp polythionates do not exist and if introduced are decomposed into sulfites and thiosulfates.[1] Any precipitated sulfur is changed by alkali into thiosulfate and polysulfide. Sulfites and sulfides react to form thiosulfate, so that in the end it is possible to have in an alkaline solution only thiosulfate and an excess either of sulfide or sulfite. Confirmatory tests were made and it was finally established that the alkaline mill pulps made from the United Verde ore contained

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[1] E. H. Riesenfeld and G. W. Feld: Polythionsäuren und Polythionate. *Ztsch. anorg. allgem. Chem.* (1921) **119**, 225.

in solution calcium thiosulfate, calcium sulfide and excess colloidal sulfur. Dithionates can also exist in alkaline solution, but tests for dithionates failed to reveal their presence.

The methods of analysis by which these reducing agents could be determined were then developed. The solution was titrated for causticity, using phenolphthalein indicator, with a standard hydrochloric acid solution, and colorimetric estimation of hydrogen-ion concentration was also made. Samples were treated with a very dilute solution of sulfuric acid to absence of pink color of phenolphthalein indicator, corresponding to pH = 8.5 and were titrated with standard iodine solution. A slightly acidified sample was titrated with standard permanganate. The permanganate oxidized both the thiosulfate and sulfide in solution, whereas the iodine oxidized almost exclusively the thiosulfate and was taken as the measure of thiosulfate present. The difference in the two titrations was therefore a measure of the sulfide content of the solution. Because of the known variability of the end products of oxidation, depending among other factors on the concentration of the solutions used, all titrations were carried out under carefully controlled standardized conditions and were calibrated empirically against solutions containing known thiosulfate or sulfide content. The xanthate content of the pulps was negligible in its total reducing effect.

Further investigation showed that on aeration of these solutions such as occurs during flotation, an increasing amount of sulfate sulfur accumulated through oxidation of the other soluble forms of sulfur present. Therefore, total sulfur was always determined in addition to thiosulfate and sulfide sulfur. Free colloidal sulfur was determined occasionally by shaking with carbon bisulfide repeatedly and finally evaporating the carbon bisulfide to leave the dissolved sulfur. This was checked against a blank test in which pure water and carbon bisulfide were used. Colloidal sulfur was found to be a minor constituent of the pulps and was usually ignored.

The discovery of the fact that part of the reducing sulfur compounds were being oxidized by air rendered necessary the determination of dissolved oxygen content and the rate at which the reducing sulfur compounds were forming in a pulp and being oxidized to sulfates. The Weinig and Bowen method of determining dissolved oxygen in cyanide solutions[2] was investigated and found to be adaptable to our conditions. Briefly, it consists in adding a known excess of indigotin disulfonate to the solution to be titrated for dissolved oxygen, and then titrating back with sodium hydrosulfite solution in absence of air. The end-point is the disappearance of the indigo color. Results were expressed in

[2] A. J. Weinig and M. W. Bowen: Determination of Dissolved Oxygen in Cyanide Solutions. *Trans.* A. I. M. E. (1925) **71**, 1018.

percentage saturation with oxygen compared to solubility of oxygen from air at the room temperature and pressure.

By using these methods a survey was made of the concentrator solutions on Sept. 14, 1928, the results of which are indicated in Fig. 1. Sample *A* was some of the ingoing mill water, consisting in part of return water recovered from the tailing thickeners and in part of fresh water. The other samples of pulp are described in connection with Fig. 1. As the samples, when taken, consisted of pulp, they had to be allowed to settle a short time before a clear solution could be siphoned off. Vacuum filtering was avoided so that dissolved oxygen would not

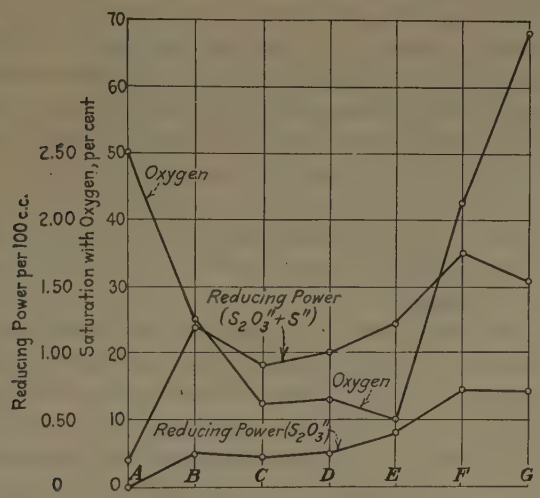


FIG. 1.—CONCENTRATOR SOLUTIONS AS OF SEPT. 14, 1928.

A = mill water
B = ball-mill discharge
C = classifier feed
D = classifier overflow
E = flotation feed
F = flotation tails
G = tailing thickener overflow

be boiled off by the vacuum. Also, exclusion of air from the sample had to be specially provided by collecting pulp into bottles filled completely to the stopper, and the clarified sample had to be titrated immediately under a cover of kerosene. Of course, time was consumed in settling before the samples of clear solutions could be withdrawn and therefore a certain amount of reaction took place between suspended minerals, dissolved oxygen and dissolved reducing agents. The data, therefore, have more relative than absolute value, but serve to give a picture of changes in the amount of dissolved oxygen and also calcium thiosulfate and calcium sulfide present in a mill pulp at various points in the flotation mill. In Fig. 1 the reducing power of 100 c.c. of solution is expressed in terms c.c. 0.0896 N $KMnO_4$ solution.

Fig. 1 shows that the water entering the ball mill and the classifier was 50 per cent. saturated with oxygen and contained a small amount of calcium sulfide. In passage through the ball mill, a considerable amount of the dissolved oxygen was used up and the pulp was only 25 per cent. saturated. Some thiosulfate was formed at this point and a considerable amount of sulfite was present in the ball mill discharge. By the time this pulp had been mixed with more water and entered the classifier most of the oxygen had been used up, in spite of the fact that the extra water, added for classification purposes, contained considerable oxygen. Evidently, the relatively quiet conditions in the classifier allowed the reducing agents in the solution and the pyrite suspended in it to use most of the oxygen, as the water was only 12 per cent. saturated while passing through the classifier, and had dropped to 10 per cent. oxygen saturation by the time it reached the flotation machines. There was a current of air through the ball mills, which accounts for the fact that the pulp issuing from the mills contained more oxygen than the pulp in the classifier, as the intense churning and beating action in the mills favored oxygen absorption.

In passing through the flotation machine, measured oxygen content of the water in the pulp increased to 43 per cent., but it is probable that the pulp at any moment in a flotation machine was actually saturated with oxygen. The time interval involved in sampling and separation of a clarified sample of water was about 15 min., and during that period much of the oxygen was used up, so that our figure of 43 per cent. saturation shows the serious difficulties in sampling. Some method of centrifuging the pulp sample to allow earlier removal of clarified solution for titration would have been better but was not at hand. Finally, the clarified water, overflowing from the tailing thickener, was 68 per cent. saturated with oxygen, although it will be noticed that it also contained dissolved calcium thiosulfate and calcium sulfide, and by the time this thickener overflow water was returned to the mill circuit, part of the oxygen, all of the thiosulfate and most of the sulfide had disappeared by interaction on one another.

The curves showing the iodine titration (calcium thiosulfate content) and the permanganate titration (thiosulfate plus sulfide content) show a gradual increase in the thiosulfate and sulfide content of the mill water as it progressed through the ball mill and through the flotation machines. The drop in sulfide and thiosulfate content of the water in the classifier feed, on calculation, was found to be entirely due to dilution with the water added to the classifier.

Anyone interested in the absolute amounts of reducing agents involved in Fig. 1 can derive them by using the following factors: 1 c.c. of the permanganate solution was equivalent to 32.2 mg. CaS per liter, or to 140 mg. $CaS_2O_3$ per liter. Thus at point *F* in Fig. 1 (flotation tailing),

the water contained $0.725 \times 140 = 101.4$ mg. $CaS_2O_3$ per liter and $(1.750 - 0.725)$ 32.2–33 mg. CaS per liter.

This formed a picture of the general changes in the flotation pulp as it progressed through the mill. Oxygen from the air is being absorbed by the water of the pulp throughout the process. Although the flotation machines are the strongest aerators, the ball mill causes a certain amount of aeration and the classifier is relatively so quiet that not much oxygen absorption takes place. Reaction is continuously taking place between the dissolved oxygen and the dissolved reducing agents and, probably also, between the dissolved oxygen and the suspended mineral sulfides. Throughout the process, soluble reducing agents consisting mainly of calcium sulfide and thiosulfate are forming, and then being destroyed by the dissolved oxygen in the pulp.

The question arose as to whether there would be any action of the solution on the sulfide minerals if there were no oxygen present, therefore tests were run in a small-batch ball mill, which was tightly closed and with air excluded. After grinding the pulp was diluted with specially boiled and evacuated water containing no dissolved oxygen, this dilution being necessary because during grinding only sufficient water was present to make a thick pulp and the latter did not permit easy sampling of the solution. By this method it was found that whenever a pyritic ore is ground in a lime solution of the concentrations commonly used in flotation, there is interaction between the mineral sulfides and the lime solution, with formation of calcium sulfide and a certain amount of calcium thiosulfate. Reference to the voluminous literature of lime-sulfur spray solutions, commonly used by the agricultural industry, will show that the formation of thiosulfate invariably accompanies the formation of calcium polysulfides.

The exact mechanism of the reaction between a solution of calcium hydroxide and the surface of a mineral like pyrite is not known to us; it was not investigated. The presence of colloidal sulfur suggests that the pyrite has probably reacted with calcium hydroxide solution to form calcium sulfide, calcium polysulfide, calcium thiosulfate, and the iron may have been converted to ferrous hydroxide. A perfectly clear filtered solution always contained amounts of iron of the same order of magnitude as the published figures on solubility of ferrous hydroxide, but this magnitude is so low that the coincidence is not put forward as evidence.

To the flotation man the fact that the surfaces of a sulfide mineral are attacked even by oxygen-free solutions of lime is of prime importance, and will better enable him to understand some of the things that go on during so-called conditioning of pulp before submitting it to flotation.

If pyrite surfaces are freshly cleaned by acid it is known that pyrite will be found above galena in the floatability series, but the actual condition of pyrite in the usual alkaline flotation pulp is one of consid-

erably depressed floatability as compared to such minerals as galena and sphalerite. Comparison of ground pyrite with ground chalcopyrite and ground sphalerite, all of the same relative fineness, showed that a much greater amount of reducing agents formed in the pyrite pulps. This explains the ease of floating chalcopyrite away from pyrite in slightly alkaline pulps. It also makes us suspect that the low floatability of normal sphalerite is due not so much to surface corrosion of the mineral particles and filming by the products of corrosion as it is to poor floatability of sphalerite itself. Under alkaline conditions, sphalerite usually must be activated with a thin film of copper sulfide, formed by interaction with copper salts.

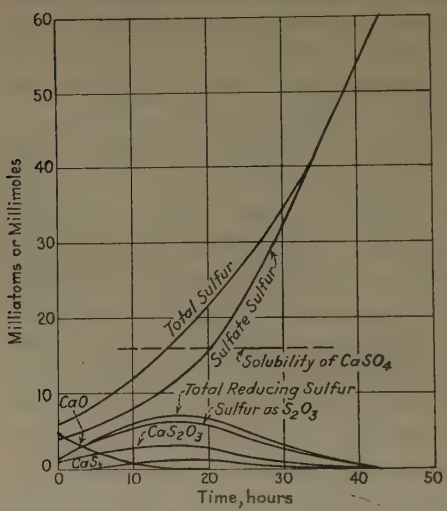


FIG. 2.—RESULT OF PROLONGED AERATION OF FINE PYRITE IN LIME SOLUTION.

Following up the data which are plotted in Fig. 1, with more precise determinations, it was decided to carry out a prolonged aeration of a sample of finely ground pyrite suspended in lime solution. In order to maintain a high oxygen concentration, pure oxygen from a cylinder of the commercial product was bubbled through the pulp. As before, the following determinations were made on samples, noting periodically the causticity, hydrogen-ion concentration, permanganate titration, iodine titration and total sulfur (by oxidation with bromine followed with precipitation of sulfates by barium chloride). From these data were derived the amounts in solution of the following compounds: calcium oxide, calcium sulfide, calcium thiosulfate, and sulfate sulfur. All of these data are plotted in Fig. 2 and are expressed as millimoles or milliatoms of the various constituents present in 1000 cc. solution up to a period of 44 hr. Samples were taken every hour in the beginning and every two to three hours at the latter half of the test.

The first important thing to be noticed is that the causticity or calcium hydrate content of the solution fell off rapidly at the beginning and more slowly later, until it vanished after 20 hr. oxygenation. The hydrogen-ion concentration (not plotted) simultaneously fell off slowly at first and then rapidly toward the neutral point, although the indicated pH when the causticity titration became zero was still 8. The colorimetric pH did not fall to a value of 7 until after 36 hr. of oxygenation and our only comment is that there must have been a certain buffering action during this stage. The indicator used for the causticity titration

was phenolphthalein, which, as is well known, has its most marked color change at a pH of about 8.4.

One of the next most important things to be observed in Fig. 2 is the fact that the calcium sulfide content in the solution reached a maximum simultaneously with the disappearance of causticity, and thereafter gradually fell off to nothing. Evidently, the presence of calcium hydroxide is necessary for the formation of soluble sulfides, and when all of the lime is used up the amounts of sulfides will decrease on account of interaction with dissolved oxygen.

Strangely enough, the calcium thiosulfate content of the solution passed through a maximum after about 15 hr. oxygenation, and was falling off when the final causticity disappeared (20 hr.), although it required 44 hr. for complete oxygenation of the calcium thiosulfate in the pulp. Possibly calcium thiosulfate is more sensitive toward oxidizing influences, under the conditions of our experiments, and requires a higher protective alkalinity. Thiosulfates are known to be unstable in acid solutions. The relative amount of thiosulfate and sulfide at the beginning of the experiment is quite interesting, as no measurable calcium sulfide was found until after about 4 hr. oxygenation. Evidently, under the intense oxidizing conditions of our experiment most of the products of reaction between lime water and pyrite are immediately oxidized, at least as far as calcium thiosulfate. It will be recalled that during the days of operation of the LeBlanc soda process the waste dumps of calcium sulfide gradually oxidized in the air so that liquors draining off them contained calcium thiosulfate.

A further point of interest in Fig. 2 is the fact that the sulfate sulfur in the pulp rapidly increased and the slope of the curve representing it also increased. Four millimoles of $SO_4$ were present in the original pulp, probably as a result of air oxidation of the pyrite before the tests were started. Additional $SO_4$ presumably originated largely from action of dissolved oxygen on dissolved reducing agents, and also from action of the dissolved oxygen on the surface of the pyrite. It is merely a coincidence that at the point where the last causticity of the pulp disappeared the amount of $SO_4$ present approached the solubility of calcium sulfate. For all time intervals above 21 hr. the sulfate sulfur must therefore have been present in the solution as sulfuric acid, ferrous sulfate, or calcium sulfate in a condition of supersaturation. Regarding the last, insufficient lime was used in the original pulp to satisfy so much sulfate sulfur, and while a certain amount of evaporation took place, thereby increasing the concentration of the dissolved materials, there was not sufficient lime to account for the great quantity of sulfate formed. This may be taken as reasonably good evidence that the dissolved oxygen in the pulp is attacking pyrite surfaces directly, as well as being used up by the soluble reducing agents in the pulp. We also conclude that the principal

$SO_4$ compound entering the pulp, after 20 hr. oxygenation, is sulfuric acid, for the reason that very little iron was present.

### *Action of Air on Pure Solutions*

As the curves in Fig. 2 showed that soluble sulfides and thiosulfates tended to form in a pulp and later tended to be oxidized to sulfates, it was felt necessary to check this observation, therefore solutions of calcium sulfide and calcium thiosulfate were prepared and treated in a similar manner by bubbling air and oxygen through them. The following results were obtained:

1. Pure solutions of calcium thiosulfate remained unchanged through aeration. When made alkaline with lime, they also remained unchanged, but when they were acidified they decomposed.

2. Pure solutions of calcium sulfide, containing a certain amount of calcium thiosulfate as unavoidable impurity, can be oxidized by aeration until nothing but calcium thiosulfate remains. During the first hour of aeration there seemed to be a slight drop in the thiosulfate content, but this was thought to be due to analytical errors and was not checked.

3. Additions of solutions of ferrous sulfate, ferric sulfate or copper sulfate to the neutral calcium sulfide solutions or thiosulfate solutions caused immediate consumption of some of the reducing agents, as should be expected. The loss in alkaline solutions is less than in neutral solutions.

4. Addition of finely ground particles of United Verde pyrite without previous washing caused either neutral or basic solutions of calcium thiosulfate to suffer an immediate increase in their reducing power. A slightly higher increase was produced in basic than in neutral solutions. On oxygenation in the presence of the particles of pyrite the neutral solutions showed a drop in both thiosulfate and sulfide content until after 9 hr. only thiosulfate was left, and with continued aeration the thiosulfate content also fell off on account of oxidation. In the basic solutions the same phenomena as those recorded in Fig. 2 took place (increase of reducing agents until the base was consumed and then a decrease).

5. Powdered chalcopyrite or sphalerite did not cause increase in reducing power of any of the solutions, but during aeration the reducing agents were oxidized. It may be concluded, therefore, that most of the generation of soluble sulfides and thiosulfates in the pulps examined was due to the presence of pyrite and also the loss in thiosulfate content during oxygenation of a neutral pulp was due to presence of pyrite.

6. The oxidation of thiosulfates in the presence of pyrite is probably due to interaction with acid resulting from oxidation of the pyrite as thiosulfate solutions are known to be unstable when acidified. An alternative explanation might be that a suspension of pyrite in a thio-

sulfate solution suffers induced oxidation similar to the induction pair, cement copper-sulfurous acid solution. By this is meant that moist cement copper alone oxidizes slowly and sulfurous acid solutions alone oxidize slowly, but when in contact with each other they are both rapidly oxidized by air. Pairs of reducing agents suffering induced oxidation by air are frequent, though not well known in chemistry. The hypothesis of induced oxidation of thiosulfates in the presence of pyrite was not tested out, for the reason that no practical value could be seen in the possible results.

### *Effect of Calcium Thiosulfate and Calcium Sulfide on Flotation*

It was at first expected that newly discovered reducing agents could be shown to have an effect on the flotation of the ore in which they formed. Blank tests, grinding some of the United Verde heavy sulfide ore without any lime, followed by adding lime, calcium thiosulfate and calcium sulfide, in controlled proportions immediately preceding flotation, showed that in the amounts measured the reducing agents add practically no effect, good or bad. We therefore conclude that these intermediate oxidation products of pyrite, which pass into the solution, are not the important results of conditioning but that the oxidized films of solid material, such as ferric hydroxide, are the important modifications produced on pyrite by the limewater and air. The reducing agents are merely results of interesting side reactions.

### *Consumption of Lime by a Sulfide Ore Pulp*

From this work on oxygenation of pyrite suspensions, it can be seen that aeration causes decrease in alkalinity of lime solutions. We have been able to segregate several causes of the consumption of lime, which are outlined herewith:

1. Reaction with metal sulfates or sulfuric acid caused by air oxidation of the ore before it is made into a pulp with limewater.
2. Reaction of lime with constituents of water. The local water is hard and to soften it with lime requires 0.36 lb. of CaO for each ton of water used; therefore, in making up a flotation pulp with 5 tons of water to 1 ton of ore a consumption of lime of 1.80 lb. is caused by the water itself.
3. During aeration some lime is consumed by $CO_2$ in the air blown into the pulp.
4. During aeration of a pulp, calcium sulfide, if present, is oxidized and as its reaction is alkaline there is an apparent loss in causticity.
5. During aeration of a pyritic pulp, dissolved oxygen acts on surfaces of pyrite and other sulfides to form metal sulfates and sulfuric acid, which react with lime.

6. Gangue constituents of the ore consume a certain amount of lime. Experiments detailed below show that both pure silica and the schist gangue in the United Verde ore consume lime. No attempts have been made to work out the exact mechanism of this consumption but it is reasonable to assume a certain amount of direct formation of calcium silicate, also a certain adsorption of lime on the surfaces of the gangue particles.

Some experiments were carried out on consumption of lime during grinding, and dilution of United Verde pyrite, chalcopyrite and several mixtures of them with quartz and schist rock. In each case a charge of

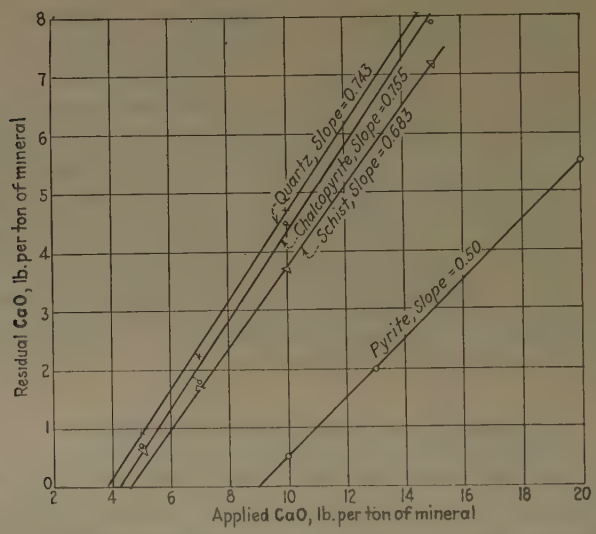


FIG. 3.—LIME CONSUMPTION WHILE GRINDING CERTAIN ORES AND MIXTURES.

mineral suitable for a flotation test in a laboratory batch machine was mixed with an equal weight of water and ground in a closed rod mill for sufficient time to give a pulp in which about 14 per cent. was caught on a 200-mesh screen, although the actual amount varied somewhat from this figure in different tests. After the grinding the pulp was diluted until it contained 5 tons of water to 1 ton of mineral and the causticity of the resultant pulp was immediately determined and compared with the amount of lime introduced during grind. Fig. 3 shows the results.

The variables in Fig. 3 are the amounts of lime introduced into the original pulp plotted as the abscissas and amounts of lime remaining in the final pulp as ordinates. The data can be well represented by straight lines for each mineral involved, and they have been extrapolated to the horizontal axis. The intercepts with the horizontal axis correspond to the

amount of lime that must be added to the ore so that after grinding and dilution a barely detectable causticity will be present. For the four minerals in question these intercepts were:

| Mineral | CaO, Lb. per Ton |
|---|---|
| Chalcopyrite | 4.3 |
| Pyrite | 9.0 |
| Quartz | 3.57 |
| Schist | 4.58 |

These values, as mentioned, are composites made up of lime consumed by the water, by the oxidation products on the surface of the minerals and by direct action with the clean minerals. As already pointed out, 1.8 lb. of lime was probably consumed by the water used in making up the pulp but the other factors are not completely determined.

The slopes of the curves in Fig. 3 are of even greater interest, in that from them are deducible the amounts of lime consumed at increasing causticities. For instance, in the curve for chalcopyrite, when 12 lb. of lime was applied to 1 ton of the mineral, suspended in 1 ton of water, ground from initial 6-mesh size until 86 per cent. passed 200 mesh and then diluted with 4 tons of water, the final pulp contained 5.8 lb. of lime. From the intercept, it is known that 4.3 lb. of lime must be used before a measurable causticity is reached, and this subtracted from 12 leaves 7.7 lb. excess lime applied to the ore, of which 5.8 lb. remained in the end—or another 1.9 lb. of CaO was used up. In other words, for every pound of excess lime added to the pulp, 0.247 lb. of lime will be consumed during the grinding of chalcopyrite. This should be a fairly good measure of the rate of the consumption of lime on a pure chalcopyrite surface in a closed mill without disturbing influences. The values are as follows for the four important minerals in the United Verde ore:

| Mineral | CaO Consumed per Pound Excess CaO Applied, Lb. |
|---|---|
| Chalcopyrite | 0.247 |
| Pyrite | 0.50 |
| Quartz | 0.257 |
| Schist | 0.317 |

If it were possible to measure the total clean surface of each of these minerals in the ground pulp, the consumption of lime per unit of surface per unit of time would be immediately derivable, but this is not possible because data are insufficient. Five minutes was allowed for the grinding of chalcopyrite, 6 min. for pyrite and 7 min. for both quartz and schist.

The consumption of lime on the quartz, schist and chalcopyrite is of the same order of magnitude, and the suggestion immediately might be made that lime disappears mainly by absorption and very little by chemical action. With pyrite, we already know that at least a portion

of the action is chemical, although there should be a certain amount of adsorption of calcium hydroxide from the pulps. The practical conclusion from all this work is that each mineral involved removes lime from its solution in the mill water in an amount depending on the amount of lime present, and that this amount is specific for each mineral.

*Lime Consumption during Flotation*

In making up synthetic pulps from chalcopyrite, pyrite, quartz and schist, the causticity of the synthetic pulp entering the flotation machine was determined and compared with the causticity after flotation. Fig. 4 shows the results.

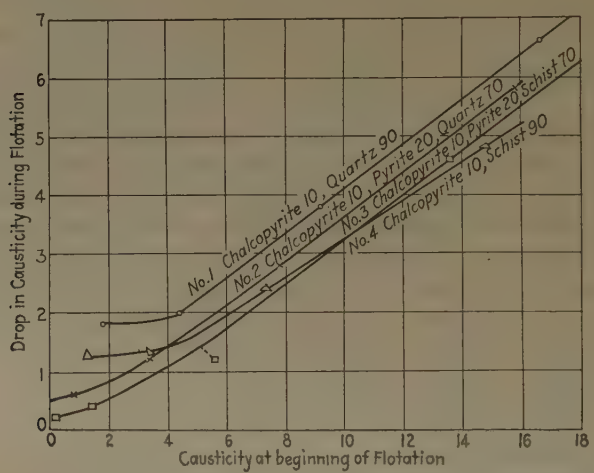


FIG. 4.—LIME CONSUMPTION DURING FLOTATION.

The original causticity titrations are plotted against the drop in causticity during the flotation for four different synthetic mixtures. In each case a flotation period lasted 7 min., and the pulp contained 5 tons water to 1 ton solids. The data in Fig. 4 can be converted to pounds per ton of lime to solids by dividing each datum by 2. They also can be converted to pounds of lime per ton of water by dividing each datum by 10. The main portions of the curves can be represented by a straight line, showing that with increasing original causticity an increasing amount of lime is consumed. The amount of air blown through the pulp during the 7 min. is not known, therefore the consumption of lime by $CO_2$ in the air cannot be calculated. The curves have approximately the same slope, so that we can say in general that for every increase of 1 lb. of lime in the pulp, 0.38 lb. is used up during the flotation by reaction with $CO_2$ in the air, and with constituents already

in the pulp, or produced by action of the air on them. The segregation of the various causes of this lime consumption was not attempted.

### *Flotation after Grinding in Oxygen*

To test the effect of excessive oxidation during wet grinding, a small laboratory rod mill was fitted with closed ends and grinding was conducted in presence of pure oxygen gas, under pressure of 25 lb. per sq. in. The resultant pulps were treated by flotation (roughing test only) in comparison with pulps prepared in the same mill without oxygen. Lime in varying proportions was used during the grinding and curves of extraction were compared as functions of lime used. The ore contained chalcopyrite, marmatite and pyrite in a schistose gangue.

The curve for grinding in presence of oxygen showed a better copper extraction in the roughing tests in all cases. The difference was greater the higher the amount of lime used, excessive lime seeming to depress flotation of chalcopyrite when ground without access of oxygen but hardly any depression being noted when oxygen was present. The same was true for marmatite extraction. Pyrite rejection on the pulps ground with oxygen present was comparatively low when small amounts of lime were used but with higher amounts of lime the pyrite rejection exceeded that possible when grinding with oxygen absent.

Evidently, on this ore it is of benefit to have oxygen present in the ball mills. While it is easy to understand why better pyrite rejection was obtained, due to corrosion of the pyrite surfaces, it is not so easy to understand why better extractions were obtained of the chalcopyrite and marmatite, and further work needs to be done. These data are presented at this time to show that the interaction of sulfide minerals, oxygen, lime and soluble reducing agents formed in the solution is of importance in the flotation behavior of the pulp. This division of the subject is worthy of an extensive paper, but its discussion will not be attempted here.

### *Conditioning in Thick and Thin Pulps*

Another series of tests was carried out with identical closed-mill grinding conditions, oxygen excluded, but the oxidation was carried on subsequent to grinding by transferring the pulp to a flotation test machine, then adding identical amounts of lime to the pulp and agitating for increasing periods of time. In one series of tests the pulp was transferred from the grinding mill with little or no dilution and in the other series of tests the pulp was diluted immediately to the degree satisfactory for flotation. We therefore conditioned the minerals in one case in a thick pulp and in the other in pulp of normal dilution. After condition-

ing, the thick pulps were diluted to the same dilution as the thin ones and subjected to flotation.

The effect which we wished to study was that of oxidation in a pulp of relatively high lime concentration as compared to one where the same quantity of lime was applied to the mineral surfaces in a much more dilute condition. Pyrite rejection in the thin pulp rose in 20 min. to a constant amount of 71 per cent., whereas after conditioning in the thick pulp pyrite rejection rose in 10 min. to a constant amount of 76 per cent. There is, therefore, a definite benefit from conditioning in more concentrated lime solutions. Marmatite extraction in the thin pulps rose to a maximum of 75 per cent. after 25 min. conditioning, whereas in the thick pulp it rose to over 80 per cent. in the same time. Chalcopyrite extraction was constant at 94 per cent. in both series.

We conclude that where alteration of the surfaces of mineral particles by action of dissolved chemicals is a prerequisite to good flotation, it will pay to condition in as thick a pulp as possible in order to use the highest possible concentration of the conditioning reagent.

## *Conclusions*

1. A study of pyritic flotation pulps made alkaline with lime has shown that in the presence of air oxygen is always dissolved in amounts depending on the amount of aeration; also, reducing agents identified as soluble sulfides and thiosulfates, with minor amounts of colloidal sulfur, are present as a result of action of lime and air on powdered sulfide minerals.

2. The dissolved oxygen and soluble sulfides react on each other with production of thiosulfate and sulfate.

3. The dissolved oxygen and thiosulfate interact in presence of powdered pyrite; at least thiosulfate disappears during oxygenation in the presence of pyrite, with formation of sulfate.

4. Causticity of such pulps drops during oxygenation and the maximum amounts of soluble reducing agents form as the causticity approaches zero, after which they also rapidly disappear and the only product of action of the oxygen on the ore pulp is sulfates, mainly sulfuric acid.

5. These effects were more pronounced in pyrite pulps than in pulps made with chalcopyrite or sphalerite.

6. A survey of the oxygen content and reducing agents in the pulp of a flotation mill has been made.

7. Lime in a flotation pulp is consumed by interaction with sulfide minerals, with gangue minerals, probably by adsorption on all surfaces, by reaction with oxidation products on the minerals produced before or during grinding and flotation, by carbon dioxide from the air coming into

contact with the pulp and by reaction with constituents of the water used. Part of these factors have been measured for the Jerome ore and Clarkdale conditions.

8. Grinding an ore in limewater with exclusion of oxygen produced a pulp which gave worse flotation results in flotation of chalcopyrite and sphalerite and rejection of pyrite than one in which plenty of oxygen was present during grinding.

9. The addition of lime to a thick pulp from a grinding mill and conditioning by aerating permitted better subsequent flotation results than adding the same amount of lime to a pulp diluted to flotation density before similar conditioning.

10. The soluble reducing agents produced by action of lime and oxygen, when introduced in controlled quantities similar to those observed in the work recorded above, showed no perceptible effect on the flotation.

## DISCUSSION

C. G. McLachlan, Noranda, Que. (written discussion).—The results obtained by the authors with lime substantiate similar work at Noranda with sodium compounds.

The Noranda concentrator was placed in operation in October, 1928, to mill massive sulfide ores of the Rouyn district, carrying copper and gold and in certain cases zinc. It was soon found that mill results were erratic and that on ore which contained less than 20 per cent. silica the mill did not check laboratory tests. For a time rapid oxidation or tarnishing of the massive sulfide ore in large-scale operations—as compared with those in the laboratory—seemed to offer a possible explanation of this discrepancy in results. Working on this assumption, it was argued that as oxygen would react with the sulfides to produce acid-forming radicals, spraying the ore with a dilute solution of sodium sulfide as it entered the mill bins should prevent such an action. Laboratory tests supported this contention and the practice was used in the concentrator with beneficial results. Conditioning tests were then run with other reagents and it was found that soda ash promised to give equally good if not better results than had been obtained with sodium sulfide. A mill test was made which showed some promise and about 10 days later experiments were carried out to determine the floatability of the fines which had been sprayed in this way. These tests gave considerably better results than those which had previously been made on absolutely fresh ore, or on ore which had been subjected for a short time only to contact with soda ash.

This result was so directly opposed to the first view that in order to investigate the variation further, charges of freshly broken ore, and of the fines which had been in contact with soda ash, were ground at 50 per cent. solids with distilled water, which was subsequently analyzed for dissolved salts. After the analysis had been made, difficulty was experienced in combining the sulfate radical and the sulfur with the sodium base in such a way as to check with the "total solids," until the assumption was made that the sulfur not combined as $SO_4$ was present as $S_2O_3$. This assumption was later confirmed by chemical tests. The compounds found in these water analyses are given in Table 1.

These results showed that oxidation had proceeded further in the case of the conditioned ore than it had with the freshly broken ore, and indicated that, contrary to the opinion previously held, oxidation of the type of ore being milled here—with free alkali present and within the limits determined by these tests—was beneficial

to flotation, and that titration of the ore pulp for sodium thiosulfate content would probably indicate how far the desired reaction had gone.

A check was made on the mill circuit for thiosulfate content and it was found that considerably less of this compound was present than had been found in any of the laboratory tests. Raising the temperature of the pulp and injecting air into it seemed the most likely way to correct this condition, and it was found that after an air agitation period of 20 min. at 25° C.—the same time as that in the United Verde's experiments—the thiosulfate content of the pulp increased until it was the same as that previously found by analysis in the water in which the fast-floating fines had been ground; further, flotation tests made on this pulp checked those obtained on the conditioned fines. These tests therefore showed that thiosulfate formation, which we considered to be a measure of the degree of oxidation of the pulp, was a gage by which the suitability of the pulp for flotation could be determined.

TABLE 1.—*Compounds in Water Analyses*

| | Fresh Ore, Grams per 100 c.c. | Conditioned Ore, Grams per 100 c.c. |
|---|---|---|
| $Na_2SO_4$ | 0.0568 | 0.3077 |
| $Na_2S_2O_3$ | 0.0192 | 0.0958 |
| $NaCl$[a] | 0.0040 | 0.0066 |
| $Na_2CO_3$ | 0.1026 | 0.1078 |
| Total, calculated | 0.1826 | 0.5179 |
| Solids, found | 0.1882 | 0.5204 |

[a] Sodium chloride was present, due to impurities in the soda ash.

The work outlined covered a period of several months. The first tests in which the ore was conditioned with a reagent for a definite period of time prior to grinding were made toward the end of December, 1928, and during January almost all the ore milled was sprayed with a weak solution of sodium sulfide as it entered the storage bins immediately ahead of the grinding circuit. At the end of January the mill was shut down, as the ore increased in grade and was sent direct to the smelter. This permitted an intensive laboratory investigation to be made of conditioning and other points connected with the treatment of the ore. As a result of certain of these tests, a 100-ton lot of ore was milled in the middle of February, to which soda ash had been added dry upon its receipt at the mill bins the previous day. The metallurgical results obtained on this ore were fair but did not duplicate those obtained in the small-scale tests. The fines, however, from this ore, when treated in the laboratory 10 days later, gave very promising results. The water analyses to investigate the reason for this improvement followed, and the first aeration tests were carried out in the laboratory in March and April. At the end of the latter month the concentrator was placed on a 24-hr. basis, and from that time until the middle of June, when the practice was temporarily discontinued to make way for other tests, all ore as it entered the concentrator bins was sprayed with a solution of soda ash containing a small percentage of sodium sulfide, but it was not until the end of July that an opportunity offered for checking up the thiosulfate content of the mill circuit. Then it was found that the concentration of this salt in the mill circuit was much less than in any of the laboratory tests, including those which had been made on freshly broken ore. Additional tests were carried out which resulted in the installation of two aerating tanks in the mill immediately ahead of flotation. These tanks improved the grade of the concentrate but laboratory tests and thiosulfate determinations showed

that a 20-min. period of aeration would be required before optimum results could be obtained. Profiting by the experiments gained in the operation of the two small tanks, one large tank divided into two sections for series treatment, and big enough to provide the necessary aeration period, was placed in operation in the mill during the third week of August. This tank was fitted with bottom bleeder pipes so that advantage might be taken of the classifying action resulting from the hindered settling effect produced by the bubbling up of the air through the pulp. The coarse sand bled from these pipes is being returned to the grinding circuit. Temperature control was provided for by injecting steam into the tank. More recently one of the two smaller tanks has been put back in the mill so that the rougher concentrates may be subjected to a second period of aeration, before cleaning. This has resulted in raising the grade of the cleaner concentrate about 1 per cent. and in lowering the cleaner tailing.

Additional laboratory tests have been made to determine what effect sodium thiosulfate and sodium sulfate have when added as reagents to samples of fresh ore. Our tests check those carried out by the United Verde Co., as better results were not obtained through the addition of these salts. On the other hand, pulp that had been conditioned ready for flotation still exhibited fast-floating properties even after being washed and floated in fresh water.

In the foregoing discussion an attempt has been made to trace the course of the research work here from a start which differed widely from that employed by the United Verde, to a point where the findings of the two investigations, despite the difference in the two reagents used, bear a marked degree of similarity. For this reason the cycle of development was first outlined and then the changes made in actual mill operations.

It may be advisable to stress the point that the use of pulp oxidation here necessitates the maintenance of a definite degree of protective alkalinity and it is probable that the beneficial effect noted as the result of the addition of sodium sulfide to the ore as it entered the mill bins depended more on the fact that this reagent gives an alkaline reaction than on its sulfidizing property.

Further experiments involving pulp oxidation, including tests with lime, are being tried, and we shall watch with considerable interest the outcome of additional work that may be carried out by the Research Staff of United Verde Co.

F. Tartaron, South Strafford, Vt. (written discussion).—Fig. 1 reveals the remarkable and seemingly paradoxical fact that the generation of soluble reducing agents takes place most rapidly under the worst conditions; that is, in the ball mill and the flotation machine, where the greatest quantity of oxidizing agent—air—is being introduced. The ball mill is an open trunnion type, readily admitting air, which is beaten into the pulp. The flotation machine is an M. S. subaeration type, utilizing large quantities of air. Yet the curves indicate that in both these machines the generation of soluble reducing agents is most rapid. A clue to the explanation of this lies in the fact that in both these places is the greatest intensity of mechanical agitation. The possibility that the rate of generation of soluble reducing agents may be a function of the intensity of agitation of the suspension suggests itself. This is well in accordance with the much observed fact in chemistry that agitation hastens chemical reactions.

The writer is familiar with the Verde mill, hence can apply this hypothesis to the entire circuit in which the observations on quantity of reducing agents and dissolved oxygen were made. Taking the curve for total reducing power (the curve for $S_2O_3$ reducing power is roughly parallel to that for total reducing power, hence the following observations apply not only to the total reducing power but to each of its constituents individually), we note that in passing through the ball mill we get the highest rate of generation of reducing agents. In the ball mill we also have the greatest intensity

of mechanical agitation. The discharge of the ball mill travels about 8 ft. to the classifier. This distance is so short and the travel so rapid that we might expect little change in the relative quantity of reducers in solution. The drop noted has been explained by the authors as entirely due to the addition of dilution water. The pulp has now arrived in the classifier and agitation is very slow, being due to the movement of the rakes of the Dorr classifier. The generation of reducing agents has also changed to a low rate. The overflow of the classifier enters a launder approximately 2 ft. wide. We have then, the overflow of a weir 8 ft. wide entering a launder 2 ft. wide. It is obvious that a great increase in velocity will take place. Moreover, the launder makes a sharp turn and there is a drop of about 3 ft. into a box before the pulp enters the flotation machine. Clearly, there has been an increase of turbulence in the pulp. Correspondingly, the curve mentioned shows an increase in rate of generation of reducers. The pulp now enters the flotation machine, where it becomes subject to the vigorous action of the impellers. A marked increase in rate of generation of reducing agents takes place. Finally the pulp enters the thickener. An almost complete absence of agitation is characteristic of this machine and we note from the curve that the rate of generation of reducers has become negative. Table 2 summarizes this relation:

TABLE 2

| Place of Observation | Agitation | Reducing Power |
|---|---|---|
| Ball mill | Greatest | Highest |
| Flotation machine | Next | Next |
| Launder to flotation machine | Next | Next |
| Classifier | Next | Next |
| Thickener | Next | Next |

The effect of the presence of oxygen does not seem great enough to obscure this relation.

On page 369 the statement is found that precipitated sulfur is changed by alkali into thiosulfate and polysulfide. We read on the following page that colloidal sulfur has been found in an alkaline pulp. Certainly, colloidal sulfur is in a fine enough state of division to permit chemical reaction if the reaction takes place at all. The two statements are contradictory and need explaining.

The authors say that when the ore is ground in the presence of oxygen, an improvement is noted in the extraction of chalcopyrite and marmatite (p. 381). It is not clear why this is so, but an explanation may lie in the fact that colloidal sulfur is present in the pulp. Of two substances of different degrees of floatability, the more floatable will replace the less floatable in a froth. Sulfur floats much more easily than chalcopyrite, hence it may be that the improvement in extraction after addition of oxygen to the ball mill is due to the oxidation, and therefore removal, of this sulfur, which under usual circumstances would replace some of the chalcopyrite or marmatite. The quantity of colloidal sulfur is indicated as small but no quantitative statement is made concerning the improvement in extraction. The plausibility of this explanation may be destroyed by quantitative considerations which the authors, no doubt, can apply.

O. C. RALSTON, Clarkdale, Ariz. (written discussion).—The confirmation of our general findings by Mr. McLachlan is particularly gratifying. Apparently the work of McLachlan and his associates is entirely independent of our own. Furthermore, they have seemingly extended the correlation of their measurements on reducing power to their commercial operation further than we have.

The value of their work and ours is to show that lime (or soda), in producing alkalinity in the flotation pulp, is active in combining with or attacking the particle surfaces of a sulfide pulp, doubtless modifying them and altering their floatability. In both cases we have studied only the soluble products of the reaction and not the solid products. Direct study of the alterations to the particles themselves would be useful.

Our study of the soluble products from these reactions is far from complete or satisfying. One is faced with identification of a host of sulfur oxygen complexes which is discouraging. A study of the action of lime on sulfur, on which there is a voluminous literature contributed by the agricultural chemists, shows that while there are numerous compounds present in lime-sulfur solutions the two most prominent ones are thiosulfates and polysulfides. With strong aeration the polysulfides are also altered to numerous intermediate products but sulfates are the end products. Colloidal sulfur is also formed from the polysulfides. The amounts of sulfides will probably vary with the oxidizing conditions and the adventitious catalysts present. We reported only thiosulfates and sulfides by quantitative methods, which are certainly none too accurate but as good as are available. Colloidal sulfur we identified only qualitatively and we are sure many sulfur oxygen complexes are also present in small amounts.

Mr. Tartaron's question about how sulfur could be present has been answered in the last paragraph. While lime solutions attack sulfur, the oxidation of the polysulfide solutions also release a certain amount of sulfur. It is no difficult flight of imagination to find lime solutions attacking pyrite, with its so-called "feeble atom" of loosely held sulfur. It may be that a lime-sulfur solution is not in stable equilibrium until there is free sulfur present, and this could provide a second way in which sulfur would be generated. The amount of sulfur present is so small that we have attached no importance to it and cannot join Mr. Tartaron in his speculation on its possible effects on the flotation.

L. Klein, Clarkdale, Ariz. (written discussion).—As I did the analytical work on which this paper is founded, I wish to add a few remarks and reply to a criticism by Professor Taggart.[4] Professor Taggart applied the methylene blue test for sulfides to a solution that he made up from ore pulp. While I have not applied the methylene blue test, I have applied the nitroprusside test for soluble sulfides, which has been standard among cyanide men for many years. The result was positive indication of the presence of soluble sulfides in our pulps. All mill solutions, if not below the limit for the test, give a positive test for sulfide with the sodium nitroprusside reagent. Tailing solutions from a schistose feed low in pyrite, as was our concentrator feed in 1928 (average for the year was 16.7 per cent. pyrite), usually gives a negative test, since there is a limit below which the reagent will not register. On the other hand, high pyrite feeds will always produce tailing solutions with sufficient sulfide to give the positive test.

Furthermore, the behavior of these solutions on strong acidification is indicative. The odor of hydrogen sulfide is frequently obtained and at other times the odor of $SO_2$. The latter comes from acid decomposition of thiosulfates, and whether $SO_2$ or $H_2S$ predominates depends entirely on the relative amounts of thiosulfates and sulfides in the solution tested. The interaction of $H_2S$ and $SO_2$ on each other in aqueous solutions also produces sulfur and water, and one must be in excess over the other to produce an odor. I have confirmed the generation of $H_2S$ on weakly acidifying certain of these solutions by boiling off through an ammoniacal cadmium chloride solution with consequent precipitation of yellow cadmium sulfide. Mill solutions treated with ammoniacal $AgNO_3$ solution precipitate $Ag_2S$, which could come from

[4] See page 238.

either sulfide or thiosulfate or both. Determination of the Ag content of the precipitate gives results when calculated to the same terms as used in the $KMnO_4$ titration, which closely check the $KMnO_4$ value. Note the following test made on a composite of mill solutions from various spots in the mill circuit:

| | |
|---|---|
| Reducing power by titration with $KMnO_4$ | = 2.3 (0.0896 $NKMnO_4$) |
| Reducing power by titration with $I_2$ | = 1.2 (equivalent to $KMnO_4$) |
| Reducing power by evolution of $H_2S$ | = 1.0 (equivalent to $KMnO_4$) |
| Reducing power by precipitation of $Ag_2S$ | = 2.2 (equivalent to $KMnO_4$) |

Therefore there is no doubt about the presence of soluble sulfides in the solutions under proper conditions, although the question could be raised easily as to whether the difference between the iodine and the permanganate titrations is entirely due to sulfides and not to a combination of sulfides and some oxysulfosalt as yet unidentified.

# Copper Sulfate as Flotation Activator for Sphalerite

By O. C. Ralston,* C. R. King* and F. X. Tartaron,* Clarkdale, Ariz.

(San Francisco Meeting, October, 1929)

The use of copper sulfate for improving the flotation behavior of sphalerite is probably at least 15 years old. The original discovery of its activating influence is somewhat obscure. The story goes that in the mill at Mascot, Tenn., its favorable action was discovered by accident, early in 1914, as follows: The original laboratory test work on a sphalerite ore gave favorable flotation results, but after a mill had been built the flotation concentration of the ore was very unsatisfactory. In diagnosing the probable reasons, one fact pointed out was that the laboratory test machine had been constructed of bronze whereas the commercial machine allowed pulp to come in contact only with wood and iron. A plate of sheet copper was hung in the flotation machine and results immediately improved. At first fanciful explanations of electrolytic and electrostatic behavior were given credence, but when the copper plate was removed and a small amount of copper sulfate substituted in the pulp an even more favorable result was obtained. Toward the end of 1914 copper sulfate was also adopted in the acid flotation circuit of the Butte and Superior Copper Co. Just who is responsible for the original discovery the present writers do not know. It seems strange that in that era of flotation litigation this discovery was not patented.

While for pragmatic purposes it may be sufficient to know that the mere addition of copper compounds to a flotation pulp is sufficient to activate the flotation of the sphalerite, for scientific purposes it is quite desirable to know more about how the action takes place. It is the purpose of this paper to present certain evidence dealing with the mechanism of the beneficial effect.

The description of the effect as *activation* in contradistinction to *depression* is now common in both the English and German languages. It makes no assumptions as to whether the zinc sulfide surfaces have been filmed with copper compounds. In fact, the principal differences of opinion expressed in the literature deal with whether there is an actual formation of CuS (or even $Cu_2S$) on the surface of the sphalerite.

Activation of sphalerite takes place in alkaline, neutral or weakly acid solutions and whereas the present day flotation of sphalerite is usually in an alkaline solution, the early use of copper sulfate was in a sulfate solution.

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*Of the Research Staff, United Verde Copper Co.

## Microscopic Examination

Some of the first to use a microscope in studying surfaces of sphalerite particles when treated with reagents were Tucker and Head.[1] Large cleavage surfaces of pure minerals were covered in half by paraffin and were attached to the impeller of a flotation machine to be immersed with proper agitation in a flotation pulp containing copper sulfate. When the paraffin film was removed, the exposed surface was found to be coated with an unknown film. This gave credence to the theory that a film probably of copper sulfide had been formed.

On the other hand, Ince[2] says that despite intensive microscopic study of sulfide surfaces after treatment in solutions more concentrated than those used in practice, there were revealed no surface alterations visible at a surface magnification of 500. Also, S. I. and A. S. Mitrofenoff[3] state that pure crystals of blende and pyrite lay in a 10 per cent. solution of copper sulfate solution without stirring for two months with no visible alteration of their surfaces.

The Mitrofenoffs noticed that if sodium carbonate were added to a dilute copper sulfate solution the blende, and to a less extent pyrite, became covered with spotty discolorations, or even radiating crystalline masses of high luster. In the presence of weak xanthate solutions, blade-shaped forms were seen on the blende grains in either acid or alkaline solutions. Therefore they formed the conclusions that the important film was cupric xanthate and their theory of activation includes primary formation of zinc hydrate, cyanide or carbonate film on the zinc sulfide surface followed by metathetic formation of the corresponding copper compounds followed by reaction with the xanthate solution to form insoluble copper xanthate. Without disputing their theory, it must be pointed out that copper sulfate has been used for an activator for many years before xanthates were adapted to flotation, and in the presence of almost every conceivable flotation oil or soluble collector.

While the work of Tucker and Head has been criticized by Taggart, Taylor and Ince[4] in such a manner as to cast serious doubt on the character of their visible films, there is one bit of forgotten evidence in the literature which gives strong probability to the existence of a microscopically invisible film of copper sulfide on the activated sphalerite surface. This is provided by Wentworth[5] who, in describing the old electrostatic

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[1] E. L. Tucker and R. E. Head: Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals. *Trans.* A. I. M. E. (1926) **73,** 354.

[2] C. R. Ince: A Study of Differential Flotation. See page 261.

[3] *Mineraljnoje Syrjo* (1928) 246, through *Metall und Erz* (1928) **25,** 644.

[4] A. F. Taggart, T. C. Taylor and C. R. Ince: Experiments with Flotation Reagents. See page 285.

[5] H. A. Wentworth: Electrostatic Separation of Minerals in Ores. *Eng. & Min. Jnl.* (1910) **90,** 15.

concentrating or separating processes, pointed out that the electrostatic separators functioned because of differences in conductivity of mineral particles. Sphalerite has low conductivity, therefore minerals of higher conductivity, such as galena and pyrite, can be separated from it, leaving the sphalerite mixed with gangue minerals. If this remaining mixture is placed in a copper sulfate solution, washed, dried and concentrated on the same electrostatic separator, the sphalerite particles will function like good conductors and will separate from the gangue. They are not visibly altered, but apparently even an invisible film of the highly conductive copper sulfide is sufficient to make them function as good conductors. After long immersion, or several immersions, the blende particles grow distinctly brown; this, of course, is not evidence proving the existence of a film of copper sulfide because some other copper compound might have been involved. The evidence, at least, supports the inference that there is a film of some copper compound.

## Typical Effects of Copper Sulfate

As an example of the beneficial effects of copper sulfate in the activation of sphalerite toward flotation, the series of results shown in Fig. 1 is of interest. These represent rougher tests on a sample of heavy pyritic

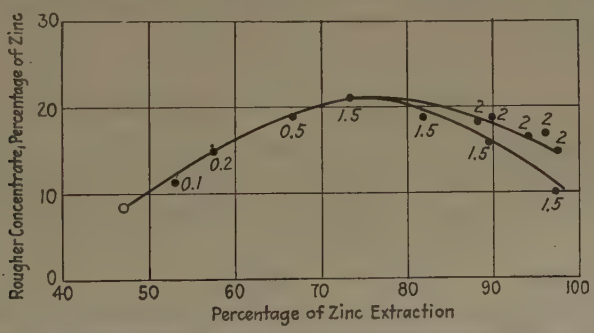


Fig. 1.—Effect of copper sulfate in roughing tests.

Amounts $CuSO_4.5H_2O$ given on diagram, in pounds per ton ore. Other reagents: 0.1 lb. pine oil; 0.1 lb. potassium amyl xanthate. Causticity: 0.25 lb. CaO per ton water.

ore from the United Verde Copper Co. mine at Jerome, Ariz. The particular sample in question contained about 5.6 per cent. zinc as marmatite, and was treated in a circuit made alkaline with lime, using pine oil as a frother and potassium amyl xanthate as a collector. As can be seen, in the blank test with no copper sulfate, less than 50 per cent. of the zinc was contained in a rougher concentrate, analyzing only 8.5 per cent. zinc. The addition of increasing amounts of copper sulfate increased both grade of rougher concentrate and extraction, until about 80 per cent. extraction was reached. For higher percentages of extraction the grade

of the rougher concentrate fell off. The proportions of copper sulfate used are expressed on the face of the diagram in pounds $CuSO_4.5H_2O$ per ton of ore. It will be noticed that most of the beneficial effect is obtained by as little as 1 lb. blue vitriol per ton of ore, although slightly improved results are obtained with up to 2 pounds.

The fact that these results were obtained in a pulp made alkaline with lime suggests that the copper sulfate added is probably not present as copper sulfate but was converted to copper hydroxide before the activation of the sphalerite surfaces. With this in mind the following studies were undertaken.

Another sample of ore of the following analysis was used:

| | Per Cent. | | Per Cent. |
|---|---|---|---|
| Cu | 3.03 | MgO | 0.43 |
| Zn | 5.85 | $Al_2O_3$ | 0.84 |
| Pb | 0.121 | $SiO_2$ | 13.29 |
| Fe | 34.00 | S | 40.75 |
| CaO | 1.18 | | |

In this ore copper was present almost entirely as chalcopyrite and the zinc as marmatite, containing slightly over 60 per cent. zinc. The bulk of the ore consisted of pyrite and the total gangue present was only 15 per cent., of which a portion is the schist with which the ore deposit is associated.

## Consumers of Copper Sulfate

Modern flotation is carried on mainly in alkaline pulp, therefore when copper sulfate is added to it there are several possible consumers or precipitants of the copper, which may be tabulated as follows:

1. Soluble constituents of the water, such as lime, calcium bicarbonate, cyanide, etc.
2. Gangue minerals (in this ore the schist absorbs copper sulfate).
3. Sulfide minerals, which interact with the copper sulfate solution.
4. Finely ground metallic iron from grinding machinery.

Even if copper is precipitated as hydroxide or basic carbonate by the pulp solution, or by carbonates in the gangue, the resulting precipitate is not completely insoluble, but has a certain minute solubility. From the physicochemical tables of Landoldt-Bornstein and the solubility tables of Seidell, it was found that the solubility of cupric carbonate at 18° C. is 0.031 part per 100 parts water, whereas the bicarbonate is soluble to the extent of 0.041 part at 18° C. and the hydroxide, 0.000650 part at 18° C. The solubility of the basic carbonate of the copper is given as 0.00026 part per 100 c.c. water. Therefore, while copper may be precipitated almost entirely by constituents of the pulp the solution will always be saturated to the extent represented by these figures.

## Consumption of Copper Sulfate in Neutral Pulp

When grinding the ore in local water, the resulting pulp was not truly neutral but slightly alkaline, the water in it having a pH of 7.6. A series of tests was run in which 2 lb. of blue vitriol, $CuSO_4.5H_2O$, was added to each ton of ore, which had been ground until about 20 per cent. remained on a 300-mesh sieve and pulped with water until there were 4 tons of water for every ton of ore. Two liter batches of this pulp were agitated from 1 to 10 min., then immediately filtered and the remaining copper determined. A blank was also run on a filtered portion of water from grinding a batch of ore and to it was added copper sulfate, resulting in a precipitate, which was likewise filtered. In Table 1 are given essential data of this series of tests. As can be seen, 1.9 lb. of the 2.0 lb. of copper sulfate was precipitated by the water filtered away from the neutral pulp, and at the end of 5 min. practically all the copper in each charge had been used up. Therefore this series was disappointing as far as showing whether the copper sulfate or copper carbonate or hydroxide interact with the zinc sulfide in the ore.

Table 1.—*Consumption of Copper Sulfate in Neutral Pulp*

| Time, Minutes | Temperature, Deg. F. | pH | $CuSO_4.5H_2O$ Consumed, Lb. per Ton |
|---|---|---|---|
| 1 | 80 | 7.5 | 1.962 |
| 2 | 80 | 7.4 | 1.831 |
| 3 | 80 | 7.4 | 1.894 |
| 4 | 80 | 7.4 | 1.870 |
| 5 | 80 | 7.4 | 1.997 |
| 8 | 80 | 7.4 | 1.997 |
| 9 | 83 | 7.4 | 1.983 |
| 10 | 86 | 7.4 | 1.996 |
| Blank | 80 | 7.6 | 1.901 |

## Consumption of Copper in Acidified Pulp

A series of tests was designed in which sufficient sulfuric acid was added to the pulp to keep copper sulfate in solution. The pH of the pulp was brought to about 6.0 with sulfuric acid and another series of tests was run using 2 lb. copper sulfate per ton of ore, as described above. The results of this series on the effect of time on consumption of copper sulfate are given in Table 2.

In this case, it will be noted that the blank test showed a consumption of only 0.185 lb. of copper sulfate, so that the remaining copper sulfate as such was available for interaction on the sulfide and gangue minerals. In this case, after only 2 min. time of contact 90 per cent. of the copper sulfate had been used up, but even after 120 min. a very small amount of

copper sulfate still remained in solution. The practical conclusion is that the consumption of copper sulfate by the ore in an acidified pulp is a very rapid reaction.

TABLE 2.—*Consumption of Copper Sulfate in Acidified Pulp*

| Time, Minutes | pH | $CuSO_4$ Consumed, Lb. per Ton |
|---|---|---|
| Blank | 6.4 | 0.185 |
| 2 | 6.0 | 1.793 |
| 15 | 6.0 | 1.922 |
| 45 | 6.2 | 1.775 |
| 90 | 6.2 | 1.950 |
| 120 | 6.4 | 1.950 |

Since in all the above tests 2 lb. of bluestone had been used for each ton of ore, it was thought best to vary the amount of bluestone and to give a sufficient time of contact (30 min.) in another series of tests in acidified pulp, which are reported in Table 3. Here again, acid amounting to 4 lb. per ton ore brought the pH to 6.0, and amounts of copper sulfate varying from 5 to 150 lb. per ton of ore were applied in the solution.

TABLE 3.—*Consumption of Copper Sulfate in Acidified Pulp*

| Temperature, Deg. F. | pH | $CuSO_4$ Added, Lb. per Ton | $CuSO_4$ Consumed, Lb. per Ton |
|---|---|---|---|
| 83 | 6.0 | 5 | 5.0 |
| 83 | 6.0 | 8 | 8.0 |
| 83 | 6.2 | 15 | 15.0 |
| 83 | 6.2 | 25 | 25.0 |
| 83 | 6.2 | 50 | 50.0 |
| 83 | 6.0 | 75 | 67.5 |
| ... | 6.0 | 100 | 82.1 |
| 83 | 6.0 | 150 | 90.0 |

In the 30-min. interval as much as 50 lb. of copper sulfate would be consumed completely and for greater quantities the consumption would be increased, but not all of the available copper sulfate was used up in 30 min. The copper sulfate consumption was increased at such a rate that it seemed to be approaching a maximum of about 100 lb. per ton of ore. The resulting solutions were found to contain both zinc and iron, so it could be concluded qualitatively that at least a portion of the copper sulfate had been used up on the sulfides of iron and zinc, probably with precipitation of a sulfide of copper and the passing into solution of zinc or of iron.

## Consumption of Basic Copper Compounds by Ore

While the work in acidified pulp is interesting, it still does not approach the conditions reached in practice where neutral or alkaline pulps are involved. A method of analysis was therefore perfected for differentiating copper carbonate and hydroxide from freshly precipitated sulfides of copper. Pulp samples could be deaerated by means of a vacuum or by blowing nitrogen through them. An air-free ammonia solution was used to leach out copper carbonate and copper hydroxide from such pulp. If air is excluded copper sulfide or metallic copper is not attacked by the ammonia solution.

A series of neutral pulp samples was prepared to which copper sulfate was added as above, with immediate precipitation of the basic carbonate of copper, and after various periods of agitation in closed bottles each was leached with air-free ammonia, whereby it was determined how much of the copper carbonate had interacted with the suspended ore, producing copper sulfide presumably as a film on the various sulfide minerals. The data of these tests are given in Table 4.

Table 4.—*Consumption of Copper Carbonate by Ore*

| Time, Minutes | Temperature, Deg. F. | $CuCO_3$ Consumed, Lb. per Ton |
|---|---|---|
| 5 | 82 | 1.754 |
| 10 | 82 | 1.833 |
| 30 | 82 | 1.881 |
| 90 | 82 | 1.983 |

This table shows that of the copper corresponding to 2 lb. original copper sulfate per ton of ore, the equivalent 1.75 lb. is used up in 5 min. and practically all of it is gone in 90 min. Therefore, in spite of the low solubility of the carbonate and hydrate of copper, each can be quite rapidly used up by the sulfide minerals of the ore. This is believed to be a definite piece of evidence, previously lacking, which shows that the copper sulfate added to an ore pulp ultimately is converted to a sulfide of copper.

## Consumption of Copper Hydrate in a Lime Circuit

A series of pulps was made up to which lime was added in amounts of 8 lb. CaO per ton of ore, causing the resulting pulp to have a pH of 11.8. To samples of this pulp increasing amounts of copper sulfate were added with instantaneous conversion of copper sulfate to copper hydrate and the samples were agitated for 30 min. in closed bottles without contact with air. Unreacted copper hydrate was leached out with ammonia and the tabulated data are given in Table 5. The copper hydrate converted into sulfide is expressed in the fifth column in pounds per ton ore for comparison with the original amount of copper hydrate added. When

compared with the series run in acid pulp there is a smaller consumption of copper. For instance, when 100 lb. of bluestone was added (equivalent to 39.0 lb. of $Cu(OH)_2$) the copper equivalent to only 30 lb. $CuSO_4.5H_2O$ was consumed by the ore in a lime circuit, whereas in an acid circuit 82 lb. was consumed by the ore.

In the last column of Table 5 are given the amounts of zinc dissolved in the ammonia solution, so that one must presume that the bulk of copper

TABLE 5.—*Consumption of Copper Hydrate in Lime Circuit*

| Temperature, Deg. F. | pH | Bluestone Used | $Cu(OH)_2$ Equivalent | $Cu(OH)_2$ Consumed, Lb. per Ton Ore | Zn in $NH_3$ Solution, Lb. per Ton Ore |
|---|---|---|---|---|---|
| 84 | 11.8 | blank | | 0.39 deducted below | Trace |
| 84 | 11.6 | 1 | 0.39 | 0.25 | 0.352 |
| 84 | 11.4 | 3 | 1.17 | 0.84 | 0.333 |
| 84 | 11.4 | 5 | 1.95 | 1.16 | 0.292 |
| 84 | 11.2 | 10 | 3.9 | 1.80 | 0.222 |
| 84 | 11.0 | 20 | 7.8 | 3.36 | 0.259 |
| 84 | 10.0 | 50 | 19.5 | 7.6 | 0.666 |
| 84 | 8.0 | 100 | 39.0 | 11.7 | 1.006 |

hydrate consumed by the ore reacted with other minerals than with the sphalerite. In the case of 100 lb. of bluestone added to the ore, of which the equivalent of 30 lb. was ultimately converted to sulfide, the actual copper involved in the 30 lb. of bluestone is 8.5 lb. and there was found in solution only 1 lb. of zinc. As they are almost of the same atomic weight, 1 lb. of copper should be replaced by about 1 lb. of zinc, and therefore out of the 8.5 lb. of copper converted to sulfide 7.5 lb. must have been used up on something else in the ore—probably pyrite. This conclusion is supported by the fact that pyrite is also activated by copper sulfate, although not in the same proportion as sphalerite.

## ACTION OF COPPER SULFATE ON PURE MINERALS

This work indicated the desirability of studying the action of copper sulfate on individual pure minerals and therefore samples of sphalerite, chalcopyrite, pyrite and barren schist were obtained for this purpose. They were placed in dilute copper sulfate solutions and allowed to stand for 24 hr. with resulting copper consumption tabulated in Table 6. In this case the copper consumed is expressed in milligrams per gram of mineral used, and again the last column contains information on the amounts of zinc or iron liberated. Ferric hydrate was plainly visible in the pulp and was extracted by a quick leach with dilute hydrochloric acid. Apparently copper sulfate is consumed by all four constituents of the ore in the following order: pyrite, chalcopyrite, schist, sphalerite. Presumably, the

copper sulfate absorbed by the schist is either precipitated by calcium carbonate or is adsorbed.

In the face of this evidence we must conclude that if sphalerite is activated by formation of a film of copper sulfide on its surface, the properties of this film must be considerably different from the properties of the films produced on pyrite and chalcopyrite. In the case of the sphalerite we can expect a cupric sulfide film and the zinc from the zine

TABLE 6.—*Action of Copper Sulfate on Pure Minerals*

| Mineral | Condition of Circuit | Copper Consumed, Milligrams per Gram of Mineral | Zn or Fe Liberated, Lb. per Ton Ore | |
|---|---|---|---|---|
| ZnS | Neutral | 3.04 | 1.06 | Zn in soln. |
| ZnS | Alkaline | 2.68 | 1.24 | |
| ZnS | Acid | 1.66 | 2.00 | |
| $CuFeS_2$ | Neutral | 6.08 | 0.00 | Fe in soln. |
| $CuFeS_2$ | Alkaline | 5.93 | 0.00 | |
| $CuFeS_2$ | Acid | 2.51 | trace | |
| $FeS_2$ | Neutral | 8.80 | | |
| $FeS_2$ | Alkaline | 9.30 | | |
| $FeS_2$ | Acid | 7.90 | | |
| Schist | Neutral | 3.70 | | |

sulfide should pass into solution as the soluble zinc sulfate or as the slightly soluble zinc hydrate. In the case of the pyrite and chalcopyrite the iron that is displaced by copper cannot pass into solution in an alkaline pulp because ferric hydroxide has an exceedingly low solubility and the probability is that the film of copper sulfide is contaminated by ferric hydroxide precipitate, so that the floatability of the filmed pyrite and chalcopyrite should be less than the floatability of filmed sphalerite.

## METATHESIS BETWEEN SPHALERITE AND COPPER SULFATE

To make certain that there is a metathetical reaction, $CuSO_4 + ZnS = CuS + ZnSO_4$, samples of pure sphalerite were ground under water and treated with copper sulfate solution for 24-hr. periods, after which the pulps were filtered and the filtrate analyzed for copper and zinc. Nearly twice as much zinc was found in solution as there was copper displaced, indicating excess zinc passing into solution over what could be expected. However, in these tests air had access to the pulp and could have caused corrosion of the sphalerite with formation of more than the expected quantity of zinc in the solution, therefore the tests were repeated in pulp from which oxygen was excluded and in which also the sphalerite received a preliminary dilute acid wash to remove all indications of oxidation. The result was about equal amounts of zinc (0.9) found in solution as compared to the copper which had disappeared.

These tests were carried on with about 2 lb. of copper sulfate per ton of ore and in no case was a film visible under the microscope or perceptible and yet the chemical evidence shows that a metathetical reaction has taken place between the zinc sulfide and copper sulfate solution.

## General Observations

The ore with which we worked contains chalcopyrite, and most flotation reagents, under conditions of low alkalinity, form a brassy chalcopyrite froth. However, after activating with copper sulfate the froth takes on a silvery appearance due to the finely ground marmatite which it carries and for clean flotation of the marmatite the alkalinity of the pulp must be increased.

It is a matter of observation on the Jerome ores that when the natural cupric sulfide, covellite (CuS), is present in the ore it is floated with difficulty. Nevertheless, our observations indicate that the film of copper sulfide on sphalerite is cupric sulfide. This anomaly is difficult to explain. The natural cuprous sulfide, chalcocite ($Cu_2S$), is known to be much more easily floatable and our tendency during the research had been to expect results to point toward the formation of a cuprous sulfide film on activated marmatite, whereas we found cupric sulfide.

Another interesting point in connection with the Jerome ores is the fact that zinc-bearing sulfide ores from near the mine-fire zones behave as though the marmatite had already been activated and require little or no addition of copper sulfate during flotation concentration. Presumably they have already received a bath in copper sulfate solution caused by the mine fires. Furthermore, ores from the upper levels of the mine, not associated with fire zones but showing enough chalcocite to indicate enrichment caused by weathering of the outcrops, are already activated when they reach the flotation machine. Presumably, the ground water passing through them has contained copper sulfate from weathering and has left imperceptible films of the sulfides of copper in every open crack and even in cleavage planes.

The copper sulfate for activation is best added to the flotation pulp after grinding but can be added to the pulp entering the grinding mill. In the laboratory, if copper sulfate was added to the pulp before grinding, about four times as great an amount of copper was needed to get the pulp to the same degree of floatability. This is easily understood because a film of copper sulfide once formed and ground off by attrition is probably inert. Only the unutilized suspension of copper hydroxide or basic carbonate remains in the pulp to activate fresh surfaces exposed by grinding. It is possible that agitation of the pulp with free access of air after the grinding operation will cause rapid oxidation and resolution of inert copper sulfide percipitate and allow it once more to react with zinc sulfide surfaces, activating them. Eventually, any compound of copper, if

present in the pulp during long conditioning, will tend to activate the sphalerite toward flotation. Only the natural carbonate minerals of copper, malachite and azurite have been tested by us in this connection and they cause relatively rapid activation but are not as efficient as the copper sulfate.

Another bit of evidence favoring the copper sulfide film theory of activation is contained in the work of experimenters of this laboratory, which will be fully discussed in another proposed paper. We were able to deactivate[6] an activated marmatite ore by treating it with a solution of sodium cyanide, a known solvent for the precipitated sulfides of copper. After the cyanide treatment the chalcopyrite in the ore could be floated in the presence of the marmatite with the ordinary flotation reagents, whereas before the treatment the marmatite was floated with the chalcopyrite. He was able to activate, deactivate and reactivate the marmatite toward flotation. A cyanide solution is more efficient than other solvents of cupric sulfide in deactivating marmatite surface because the copper goes to form a very stable cuprocyanide ion from which it is precipitated as sulfide only with difficulty. This is very strong circumstantial evidence that the mechanism of deactivation is the dissolving away of a cupric sulfide film.

## Conclusions

We feel justified in the following conclusions:

1. Copper sulfate, when used as an activator in flotation of sphalerite, forms an invisible but physically detectable film of cupric sulfide on the surface of the sphalerite particles, as evidenced by increased electric conductivity, by chemical metathesis and by the ability to deactivate with solutions of alkali cyanides, which are known as solvents of copper sulfides.

2. Pyrite, chalcopyrite and some of the gangue minerals likewise consume copper sulfate.

3. In neutral or alkaline pulp the first reaction is precipitation of basic copper carbonate or copper hydroxide and it is these slightly soluble precipitates which are present in solution and suspension during the real activation.

4. The time necessary for efficient activation by copper sulfate, hydrate or basic carbonate is only about one minute, although to provide good mixing or stirring it is probably wise in any flotation machine to allow as much as five minutes.

5. Evidence has been presented to show that most of the copper consumed by sulfide ore is converted to cupric sulfide, through only a portion of the copper sulfide is filmed on the zinc sulfide.

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[6] Patent applications are being made on inventions involving this discovery.

6. While the flotation of pyrite is activated by copper sulfate, it is not so highly activated and a theory is presented to explain this fact.

7. Whether the increased flotation of the activated particles is due to superior floatability of the sulfides of copper or to the tendency of the flotation collector to form a compound with copper, thereby "greasing" the particle surface, is unknown but for the purposes of the present investigation it seems reasonable to claim that one important step in activation consists in filming zinc sulfide with copper sulfide.

## DISCUSSION

O. C. Ralston (written discussion).—Since writing the paper on Copper Sulfate as Flotation Activator for Sphalerite, I have been informed by A. J. Monks, of Santa Barbara, Chihuahua, that he was working at the Broken Hill Proprietary mill in Australia, about 1911, when Leslie Bradford first tried copper sulfate as a sphalerite activator at that mill. It was recognized then as a successful activator, but as an acid circuit was in use it was practically impossible to keep pyrite out of the concentrate, and the copper sulfate was therefore of value only for ores low in pyrite.

[For further discussion see page 413.]

# Activation of Sphalerite for Flotation

By Oliver C. Ralston* and Wm. C. Hunter,† Clarkdale, Ariz.

(San Francisco Meeting, October, 1929)

During experimental study on the separation of a zinc concentrate from the heavy sulfide ores of Jerome, Ariz., a great deal of attention has been given to proper activation of the sphalerite content of the ore. The sphalerite at Jerome contains enough iron to class it as a marmatite, as picked specimens have only about 60 per cent. zinc, whereas pure zinc sulfide contains 67 per cent. zinc. This marmatite in large pieces is black in color, but in dry powdered state is brown. A flotation froth made from it has a silvery black luster in comparison with a brassy luster caused by chalcopyrite which occurs in the same ores.

The sample used in most of the experiments described below consisted of about 3000 lb. of diamond-drill core from the zinc-bearing orebodies of the United Verde mine, and had the following analysis:

| | Per Cent. | | Per Cent. | | Oz. per Ton |
|---|---|---|---|---|---|
| Cu | 0.695 | $Al_2O_3$ | 0.83 | Ag | 1.30 |
| Zn | 6.17 | S | 43.35 | Au | 0.02 |
| Fe | 36.23 | CaO | 0.46 | | |
| $SiO_2$ | 9.27 | | | | |

Mineralogically, this analysis is calculated to the following, which is in agreement with the microscopic examination:

| | Per Cent. | | Per Cent. |
|---|---|---|---|
| Chalcopyrite | 2.0 | Schist | 3.2 |
| Marmatite | 10.32 | Quartz | 8.2 |
| Pyrite | 73.0 | Calcite | 0.9 |

All samples were ground in a laboratory ball mill in order to leave about 3 per cent. on a 200-mesh sieve, fine grinding being essential to liberate the minerals in the ore. Most of the Jerome ores are so intimately crystallized that reasonably complete unlocking by grinding does not take place until 800 mesh is approached. Therefore, the 200-mesh grind adopted contains a considerable amount of locked mineral grains, but not so much as to render impossible the preparation of commercial grades of concentrate.

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* Director of Research, United Verde Copper Co.

† Flotation Engineer, United Verde Copper Co.

A previous publication[1] has presented evidence that in the activation of sphalerite with copper sulfate previous to flotation a film of cupric sulfide is formed on the surfaces of the zinc sulfide particles. Following out this theory of filming, the work described in the present paper was done, about two-thirds of which involves the use of various kinds of copper compounds as activators.

## Cupric Sulfate as Activator

In the previous paper, it was shown that cupric sulfate solution reacts immediately with the water or the lime solution used for flotation, producing a precipitate of cupric basic carbonate, or cupric hydroxide, both of which are slightly soluble in lime solution, and that the cupric ions are replaced by zinc ions from the surfaces of the sphalerite particles, thereby forming a film of cupric sulfide. In Fig. 1 are given the analyses

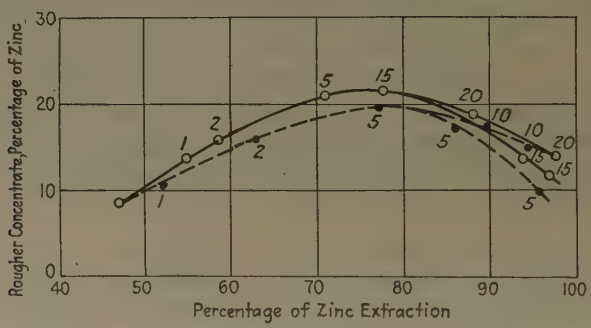


Fig. 1.—Recovery vs. grade of concentrate in activating tests.
Solid lines, $CuSO_4.5H_2O$ in increasing amounts.
Dotted lines, $Cu_2Cl_2$ in NaCl brine, in increasing amounts.
Figures refer to 0.1 lb. of activator added.

of rougher concentrate and corresponding recoveries in a series of flotation tests in which increasing amounts of copper sulfate were added to a flotation pulp ground as described above, and with sufficient lime present to give a causticity titration from 0 to 0.25 lb. CaO per ton of water when the pulp contains 4 tons of water per ton of solids. The solid line in Fig. 1 gives these data and the figures opposite each point are the units of 0.1 lb. $CuSO_4.5H_2O$ per ton of solids. Starting with the blank test in the extreme left of the diagram, increased extractions and increased grades of concentration were obtained until 1.5 lb. of blue vitriol had been added. From this point on, by suitable adjustment of lime content, increasing extractions were obtained at the cost of grade of concentrate without further addition of blue vitriol. If, however, the blue vitriol addition were increased to 2 lb. per ton, increase in extraction could be obtained without

[1] O. C. Ralston, C. R. King and F. X. Tartaron: Copper Sulfate as Flotation Activator for Sphalerite. See page 389.

as great a sacrifice in grade of rougher concentrate. Beyond 2 lb. addition, little improvement in flotation results was possible. The method of operation of the testing machine was to add the lime to the ore before grinding in a laboratory rod mill, using about 1 ton of water per ton of ore in the mill. The pulp was washed into the flotation machine and diluted to a 4 to 1 ratio water to solids, the copper sulfate was added and allowed to react for 1 min., after which 0.1 lb. of pine oil and 0.15 lb. potassium amyl xanthate were added for every ton of solids and flotation concentration was allowed to proceed for 10 min. with a constant rate of removal of froth by means of a paddle. This schedule of operation was adhered to throughout all of the tests described below.

## Effect of Cuprous Salt on Flotation

If a cuprous salt were substituted for a cupric salt, one might expect the formation of cuprous sulfide as a film on the sphalerite particles instead of cupric sulfide. The natural cuprous sulfide, chalcocite, is easily floatable, whereas the natural cupric sulfide, covellite, is not so easily floated. The cuprous sulfide is probably more metallic in nature; it certainly possesses a more metallic luster in comparison with the sooty covellite. It was therefore anticipated that by substitution of cuprous salt for the cupric salt an improvement in flotation results would be obtained. The results of a series of tests using cuprous chloride included in a solution of sodium chloride are given in the dotted lines in Fig. 1 in comparison with the results produced by the use of cupric sulfate. It can be seen that the results are almost identical with those produced by cupric sulfate with the exception that the grade of concentrate is slightly lower for any definite extraction of zinc and also that less cuprous chloride is necessary to produce a definite extraction. Since 1 lb. of bluestone crystals contains 0.255 lb. copper and 1 lb. of cuprous chloride contains 0.642 lb. copper, 1 lb. of cuprous chloride contains the same amount of copper as 2.52 lb. of bluestone. As can be seen from the points in Fig. 1, 1 lb. of cuprous chloride gave almost the same results as 1.5 lb. blue vitriol. We therefore conclude that as far as a comparison between the two activators is concerned, the only thing that is of importance is the amount of copper used. However, it is not correct to conclude that a film of cuprous sulfide is no more efficient than a film of cupric sulfide, for the reason that the amount of oxygen dissolved in 4 tons of water is more than sufficient to oxidize the copper in 1 lb. of cuprous chloride to the cupric condition. It is probable, therefore, that the copper ions actually reaching the surfaces of the marmatite particles were cupric ions. While it might be practical to deoxygenate a flotation pulp before adding cuprous chloride activator this experiment was not attempted.

Cuprous chloride is only slightly soluble in water and, as mentioned above, was included in experiments outlined in Fig. 1 as a solution in

concentrated sodium chloride brine. Results of further experimentation on the use of cuprous compounds as activators are plotted in Fig. 2. The curve drawn through the black dots is the same cuprous chloride in sodium chloride brine as is shown in Fig. 1. The curve determined by the circles is obtained by the use of cuprous chloride dissolved in a strong ammonium chloride brine. This curve is slightly above that produced by the sodium chloride brine and at its right end exceeds in grade of concentrate at a definite extraction the results obtained with cupric sulfate. The ammonium chloride brine is a somewhat better solvent for cuprous chloride than is a sodium chloride brine and presumably has caused the formation of a more finely divided cuprous hydroxide precipitate when the solution is introduced into limewater.

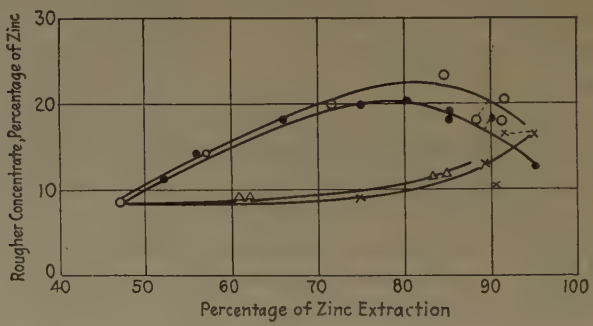


FIG. 2.—RECOVERY VS. GRADE OF CONCENTRATE FOR CUPROUS ACTIVATORS.
Dots refer to cuprous chloride dissolved in NaCl brine; circles to cuprous chloride in $NH_4Cl$ brine; crosses to cuprous chloride in $NH_4OH$ solution; triangles to cuprous chloride in NaCN solution.

Cuprous chloride is also soluble in solutions of ammonia and of sodium cyanide. It was therefore tested as an activator in such complex solutions and the results are plotted for comparison in Fig. 2. The curve through the points represented by crosses is for increasing amounts of cuprous chloride dissolved in ammonia. It follows a course radically different from the most of this type of grade vs. extraction curves. With increasing amounts of cuprous chloride up to 1 lb. per ton, steadily increasing grades and extractions were produced; beyond this amount no further benefit was noticed. With cuprous chloride dissolved in a cyanide solution (see the points represented by triangles in Fig. 2) practically identical results were obtained.

In the case of cuprous chloride dissolved in ammonia or in sodium cyanide solution, there was some question whether it stayed in solution when introduced into the limewater, therefore blank tests were made in limewater of the same causticity. The solution became opalescent but the precipitated copper hydrate was so finely divided that considerable discussion arose as to whether it had been completely precipitated. How-

ever, on standing over a week-end all of the copper "hydrate," of an azure color, sedimented, leaving a clear liquid which gave no test for copper with ammonia. It should be remarked that it was difficult to exclude oxygen from the solution of cuprous chloride in ammonia and the typical blue color of the cupric solution was always present. We presume that on account of the large amount of oxygen in the limewater all of the cuprous ion was oxidized immediately to cupric, in the case of the ammonia solution. However, against this presumption must be recorded the fact that the activation produced a much more profound effect on extraction than it did on grade of concentrate as compared with the previous results received with cuprous compounds. It is possible, therefore, that not all of the cuprous ion was oxidized during the period of time allowed in the experiments. This is especially possible in the case of the cyanide solutions.

## Effects of Time of Conditioning

Whereas in the experiments described only 1 min. was allowed for activation, it was thought that there might be a possibility of increasing the activation by permitting a sufficiently long period of time in which the cupric hydroxide precipitate could dissolve to the extremely slight amount permitted by its solubility and then react with zinc sulfide surfaces. The general idea was that the effective activation might be taking place with only a small amount of the total copper. Using 2 lb. of copper sulfate per ton of ore and periods of time from 1 min. to 60 min. practically identical flotation results were obtained, which departed by only 1 or 2 per cent. from the circle shown in Fig. 3. Evidently ample copper was available for activation even in 1 min. Therefore, a second series of tests was made in which only 0.5 lb. blue vitriol was used. The effects produced by various periods of time of conditioning are shown by the line in Fig. 3, commencing at 1 min. and ending with 240 min. It will be noticed that 5 min. conditioning time gave a somewhat enhanced result but that 15 min. gave an almost identical result with the 1-min. test. Thereafter, the grade of rougher concentrate in zinc increased with time at the expense of the zinc extraction. Apparently, with careful manipulation 0.5 lb. of blue vitriol is sufficient to

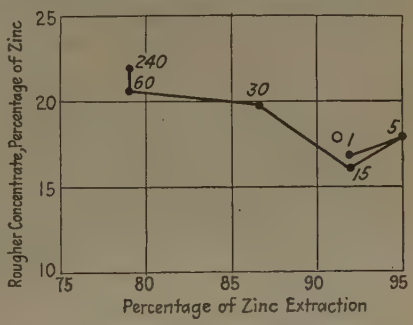


Fig. 3.—Effect of time of conditioning on activation.

Tests with 0.5 lb. $CuSO_4.5H_2O$ per ton ore. Causticity, 0.24 lb. CaO per ton water. Figures are minutes conditioning time. Circle is result when 2.0 lb. $CuSO_4.5H_2O$ is used, irrespective of time of conditioning.

produce the same activation as 2 lb. of it, but the effect is spoiled to an increasing extent by agitation and aeration beyond 15 min. time.

Just what spoils the effect can be explained in several possible ways. First, it might be assumed that the dissolved oxygen in the pulp is oxidizing away the film of cupric sulfide. If so, it should go into solution and be available for reprecipitation on zinc sulfide surfaces. However, in our previous paper we mentioned the fact that copper sulfate is also precipitated by pyrite, and as the bulk of the ore being tested was made up of pyrite any copper oxidized away from activated sphalerite surfaces could be reprecipitated on the pyrite, therefore the oxidizing hypothesis has argument both for and against it. Secondly, the decrease in extrac-

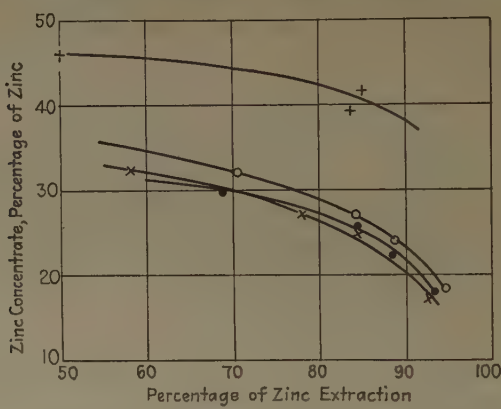


FIG. 4.—CLEANING AND RECLEANING ROUGHER CONCENTRATE.

Dots: cleaning (in three fractions) after making rougher concentrate with 1 lb. $Cu_2CL_2$ in NaCl activator.

Circles: duplicate test.

Crosses, lower curve: cleaning in three fractions after roughing with 2 lb. $CuSO_4.5H_2O$ activator.

Crosses, upper curve: cleaning and recleaning after roughing with 2 lb. $CuSO_4.5H_2O$ activator.

tion with time of conditioning might be explained on the assumption that the film producing activation is fragile and easily abraded away by agitation of the pulp. The density of the film on the pure marmatite particles is probably greater than on middling particles, therefore a middling particle losing a part of its film suffers a greater chance of being lost in tailing. This would explain the rise in grade of concentrate during the decrease in extraction resulting from long periods of conditioning.

It is hard to see how the results in Fig. 3 can be explained by any other of the activation hypotheses which have been presented. To date, the filming hypothesis seems to hold the floor.

Tests were carried out with some of the above rougher froths, giving them a cleaning treatment, and some received also a recleaning treatment.

The purpose was to study the rise in grade made possible coincident with definite amounts of extraction when the activated sphalerite was further treated. Each of these tests lasted 10 min., therefore each activated particle that was floated had been subjected to flotation conditions for a maximum of 20 min. total time. A great part of the material floats during the first 3 min. of a 10-min. test, therefore the larger proportion of the material had agitated and aerated in the flotation machine about 6 min. only. However, one might expect a certain loss in extraction with this increased period of aeration as compared with the rougher tests. The curve in Fig. 4, passing through the dots, was made by a single cleaning treatment of rougher concentrate produced by 1 lb. of cuprous chloride dissolved in sodium chloride. During cleaning, the clean concentrate was taken off in three fractions, so that the dot farthest towards the left represents the first cleanest fraction, the second dot represents the results obtained by combination of the first and second fractions, the third dot represents the results obtained by adding all three fractions of the froth together, and the fourth dot, which is farthest toward the right, represents the calculated original rougher concentrate.

The curve passed through the open circles in Fig. 4 is a duplicate test made for the purpose of determining the reproducibility of a roughing and cleaning test. As can be seen, for a given extraction the various grades of cleaner concentrate are about 2 per cent. higher than in the first test. The curve passed through the crosses is almost identical with the curve passed through the dots, but was produced by the use of 2 lb. blue vitriol during the roughing treatment. Again, to all intents and purposes, the use of cupric and cuprous salts gave practically identical results per pound of copper involved. The upper curve, delineated by three plus signs, represents the concentrate produced by roughing with 2 lb. of blue vitriol, followed by cleaning and recleaning.

## Organic Salts of Copper as Activators

While it has been assumed that the first film produced on marmatite in this ore is a cupric sulfide film, it is entirely possible that it is later altered by the potassium amyl xanthate to a cuprous amyl xanthate film. This hypothesis was tested by using cuprous amyl xanthate prepared separately as a combined collecting and activating agent.

The cuprous amyl xanthate used was an insoluble powder which was stirred into the pulp. It was felt that while its solubility was very low the solution would come in contact with zinc sulfide particles and the copper be replaced by zinc, thus filming the zinc sulfide surface with copper sulfide and also a precipitate of zinc xanthate which would be intimately entangled with the copper sulfide and tend to be water-repellent. Practically no concentration took place when pine oil was used as frother and

cuprous amyl xanthate as combined activator and collector of marmatite. Only when a solution of potassium amyl xanthate was added as collector did appreciable concentration take place and in addition a solution of copper sulfate had to be added before acceptable extractions and grades of rougher concentrate could be produced. Evidently, when solutions of copper sulfate and potassium amyl xanthate are added separately to an ore pulp they function in a different fashion from their ultimate reaction product, cuprous amyl xanthate. Our usual procedure was to add the cupric sulfate solution to the ore pulp and stir for 1 min.; the xanthate solution was then added, and finally pine oil, to produce a froth. This gave an opportunity for the copper sulfate to react with the lime-water in the pulp to produce cupric hydroxide, followed by filming of the zinc sulfide particles with cupric sulfide by direct metathesis—all this

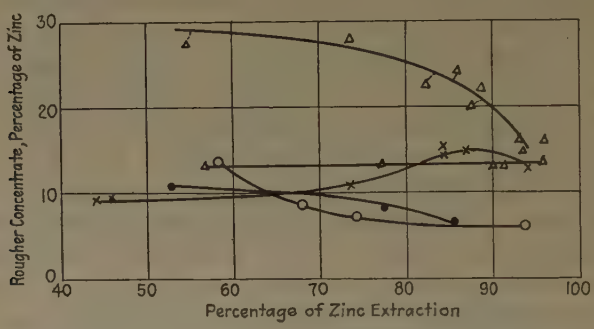


FIG. 5.—ORGANIC SALTS OF COPPER AS ACTIVATORS.

Dots: copper oleate.
Circles: copper resinate.
Crosses: triethanol amine cupric chloride.
Triangles, lower curve: roughing with copper aniline chloride.
Triangles, upper curve: roughing and cleaning with copper aniline chloride.

taking place before xanthate was added. What happens on the addition of xanthate as collector we do not know. It is certain that suspended particles of cuprous amyl xanthate in the ore pulp are of little value as activator or collector, either due to insolubility or to slow reactivity.

To further test the hypothesis of forming organic copper salts as films on the marmatite particles, a series of other organic compounds of copper were tested and the results are plotted in Fig. 5. For instance, using copper oleate one might expect that this slightly soluble salt, if it were acted upon at all by zinc sulfide, would produce a film of copper sulfide on the marmatite and that the zinc oleate resulting would also remain as a film mixed with the copper sulfide. The surface would thereby be greased effectively and should be subject to flotation concentration. In Fig. 5 the curve passing through the dots was made with copper oleate, the point farthest to the left being a blank without any activator or collector and the other two points being increased amounts of

copper oleate as combined activator and collector. It was found necessary to add small amounts of xanthate to act as a collector, because none of the organic copper salts alone provided sufficient collecting power. While copper oleate caused an increase in extraction the grade of concentrate fell off so that practically no concentration was effected. The analyses of the concentrates were almost identical with that of the original ore. If activation was taking place it was nonselective.

The same results were obtained with copper resinate, of which the curve is represented by the circles in Fig. 5. Both the resinate and oleate had to be dissolved in benzene in order to be dispersed through the flotation pulp. Both gave froth which was extremely heavy, tough and dirty and the results were totally uncommercial.

The reaction product produced by treating triethanolamine with cupric chloride solution was tested and the results are represented by crosses in Fig. 5. Increased amounts caused increased extraction of the zinc without much increase in grade until 75 per cent. extraction was approached, beyond which the grade was increased perceptibly, but the results are nowhere as favorable as those produced by ordinary copper sulfate activation.

Copper aniline chloride is another compound which was tested and which gave reasonably satisfactory results. It and others of the compounds produced from the organic bases with cupric chloride have been patented by R. B. Martin.[2] The results of rougher tests are represented by the horizontal line through triangles in Fig. 5. The ground sample of ore being tested had oxidized slightly so that the point farthest to the left was somewhat slightly activated in comparison with the usual blank on this ore, as represented by the crosses farthest to the left. Amyl xanthate had to be added as a collector during these tests and the copper aniline chloride functioned merely as an activator. Without the amyl xanthate very low recoveries were obtained. At the right end of this line on the diagram, passing through the triangles, the grade of concentrate and extraction is quite acceptable in comparison with the work of copper sulfate. Therefore, two fractionated cleaning tests, comparable with those shown in Fig. 4, were carried out and are shown by the upper line passing through triangles in Fig. 5. Compared with the cleaning tests in Fig. 4, it can be seen that the grade of concentrate produced for any definite extraction is about 2.5 per cent. lower than when copper sulfate was used as activator. This is not a great difference, therefore it is concluded that once more the important thing is the amount of cupric ion available and not the acid radical to which it is attached. In fact, having the copper attached to various organic radicals is likely to introduce into the pulp a reagent that causes nonselective flotation.

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[2] U. S. Patent 1686529, Oct. 9, 1928.

## Miscellaneous Inorganic Salts as Activators

Since salts of copper have functioned so successfully for filming zinc sulfide to produce its activation toward flotation, salts of other metals lower in the electromotive series than zinc were likewise tested. Results on several of these are plotted in Fig. 6, whereas the results on several others were not plotted.

Mercury is sufficiently below zinc in the electromotive series to be rapidly and completely precipitated by zinc from its solutions, and it was therefore expected that solutions of mercury should be efficient in filming zinc sulfide particles with the sulfides of mercury; also, it is known that the natural mercuric sulfide, cinnabar, is one of the most easily floated sulfide minerals. The results in Fig. 6 are therefore of interest.

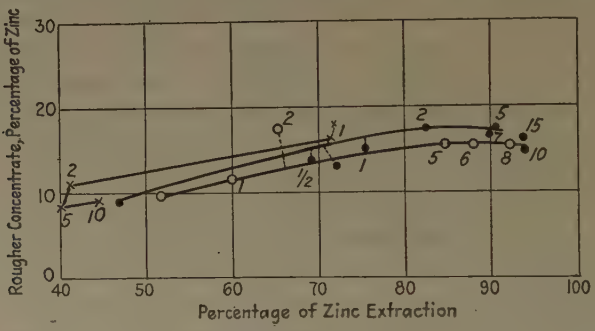


Fig. 6.—Miscellaneous inorganic salts as activators.
Dots: mercurous chloride as activator.
Circles: mercuric chloride as activator.
Crosses: cadmium chloride as activator.
Figures on plot, units of 0.1 lb. of reagent used.

The curve represented by dots is for increasing amounts of mercurous chloride used as an activator and the figures on the plot represent units of 0.1 lb. of reagent used per ton of ore. The curve does not have as pronounced curvature nor as high grade of concentrate at medium extractions in the plot as do the copper sulfate and cuprous chloride curves, but for the higher extractions the grades of concentrate are comparable with those produced by copper sulfates. The same is true for mercuric chloride as an activator, as shown by the curve passed through circles. The mercurous and mercuric salts give almost identical results, and again we suspect the oxidation of the mercurous ion to mercuric condition by the dissolved oxygen in the pulp. Since nearly 1 lb. of these salts is necessary to produce the same effect as 1 lb. of cuprous chloride or 2 lb. of cupric sulfate, the higher cost of the mercuric salts will probably make them of no value as activators. If, however, means could be found for making one unit of one the mercuric chlorides do 10 times the work of one unit of copper sulfate, there might be possibilities of economy.

Lead acetate was tested as an activator with practically negative results. Lead is nearer to zinc in the electromotive series and apparently it is not being precipitated as the easily floatable lead sulfide on the surfaces of the zinc sulfide particles.

Cadmium chloride was tested as an activator with the results shown by the crosses in Fig. 6. The sample used had been ground for some time and was slightly activated by the oxidation of the copper minerals contained in it, so that blank test gave unusually high recovery and grade of concentrate. With increased additions of cadmium chloride the grade and extraction were both depressed profoundly. Zinc salts are also known to be depressants for the flotation of zinc sulfide and apparently cadmium ions are acting in the same way as zinc ions.

Silver nitrate was likewise tested as an activator with results that are best shown in Table 1.

TABLE 1.—*Results with Silver Nitrate as Activator*

| $AgNO_3$, Lb. per Ton | Zinc Extraction, Per Cent. | Zinc Concentration, Per Cent. |
|---|---|---|
| None | 35 | 8 |
| 0.5 | 76 | 13 |
| 1.0 | 69 | 16 |
| 2.0 | 41 | 13 |
| 4.0 | 32 | 7 |

Its addition in small amounts activated the marmatite favorably, the principal effect being increased extraction. However, increasing amounts of silver nitrate depressed extraction from the optimum possible with an intermediate amount of the reagent, simultaneously raising the grade, as is usual when extraction is being gradually depressed. With still greater amounts both extraction and grade suffered and the effect was similar to that of the cadmium salt. It is possible that with the copper or mercury salts similar effects of large amounts of activator would be found, but silver salts were the only ones tested from this standpoint. The most favorable effect demanded too much silver salt to be of value commercially, so further tests were abandoned.

The effects of these various metallic salts, whose cations should be dischargeable by zinc, may be summarized qualitatively in Table 2. This table is arranged roughly as an electromotive series, showing that for metal salts of the ordinary commercial acid anions the cations have activating effects increasing along the electromotive series from silver up to copper, where the optimum effects were observed. On reaching lead no effect was observed, whereas cadimum and zinc were active poisons.

The conditions used in the tests were as follows: alkaline (with lime) pulp, 1 to 5 min. time of contact, use of potassium amyl xanthate as col-

TABLE 2.—*Effects of Metallic Salts of Which Cations Should be Dischargeable by Zinc*

| Cation Used | Activation in | | Remarks |
|---|---|---|---|
| | Grade | Extraction | |
| Silver | Slight | Fair | Excess caused depression. |
| Mercurous | Fair | Good | Probably oxidized to mercuric. |
| Mercuric | Fair | Good | |
| Cuprous | Good | Very good | Probably oxidized to cupric. |
| Cupric | Best | Best | Slightly better than cuprous. |
| Lead | None | None | Practically inert. |
| Cadmium | Depressed | Depressed | |
| Zinc | Depressed | Depressed | |

lector and pine oil for frother. These flotation conditions are known to be well suited to copper mineral flotation. Other conditions might permit some of the other cations to show up better. The superiority of the copper salts might be ascribed to numerous causes:

1. Copper xanthate films may be the least soluble.
2. Copper xanthate films may be the easiest to form.
3. Copper sulfide films may be the best adherent.
4. Solubility of cupric hydroxide may be the most favorable.

Whatever the cause, tests having shown that under present conditions no other metal salt had any advantage over copper as an activator, the subject was dropped. It is a coincidence that the activator so far best suited to the purpose was the one first found.

## SUMMARY

1. Using flotation conditions well adapted to use of cupric sulfate as a collector of marmatite into a flotation froth, it was found that cuprous salts gave no improvement in performance and pound for pound of contained copper the same results were obtained whether cupric or cuprous copper was used. This might be explained by oxidation of cuprous to cupric condition by dissolved oxygen in the ore pulp.

2. Mercuric and mercurous salts were also activators of about equal power, but were not as good as the copper salts.

3. Starting with cupric copper and passing to silver in the electromotive series the activating effects decreased, especially with respect to the grade of rougher concentrate produced. Starting with copper and going the other direction in the electromotive series as far as zinc, lead salts are inert, cadmium salts are toxic and zinc salts more toxic.

4. Copper salts of organic acids, such as oleates, resinates and xanthates of copper, fail to function satisfactorily as combined activators and collectors—at least those so far tested by methods favorable to cupric sulfate as an activator have been unsatisfactory.

5. The best activator found for flotation of sphalerite (marmatite) is the one commonly in use, copper sulfate.

6. No matter in what form the copper was introduced into the alkaline pulp it was found to be immediately precipitated as either carbonate, hydrate or basic sulfates or carbonates, these being slightly soluble precipitates which nevertheless seem to be the actual activators that react with the zinc sulfide particles to form films of cupric sulfide.

## DISCUSSION

[This discussion refers also to the paper by O. C. Ralston, C. R. King and F. X. Tartaron, which begins on page 389.]

R. Macfee, Villemagne, Gard, France (written discussion).—The subject of the activation of sphalerite for flotation is one that has been of great interest to me for some time and I have done some test work on the problem. These two papers have therefore been read with particular interest.

The ore I have to work with assays about 3 to 4 per cent. Pb; 6 to 8 per cent. Zn; 2 per cent. Fe. The ore coming from the mine is rather badly oxidized and in some cases as much as 10 per cent. of each metal has been found in an oxidized state.

The bulk of the lead is present as galena. The sphalerite varies from a very dark blende (black jack) to very pale straw yellow (amber jack). The oxidized zinc minerals are carbonates and silicates and there are traces of zinc sulfate. A small amount of pyrite also is present.

In milling, the ore is ground to 75 per cent. −200 mesh and a differential float made in a soda circuit, using Aerofloat for the lead flotation. No zinc depressants are found necessary in the lead rougher circuit but a very small amount of these agents (cyanide and zinc sulfate) are used in the cleaning of the rougher lead concentrate. It is thought that there is sufficient depressant (zinc sulfate) in the ore itself for the first rough differentiation. Most of the blende that floats with the galena in the roughers is of the lighter colored varieties.

The zinc float is preceded by conditioning with copper sulfate, xanthate and pine oil being used as frothers. The mill results have not been good; the tailings assay high in sulfide zinc.

A point of interest in the ordinary conditioning with copper sulfate noted here is that if the copper sulfate is added after contacting with extra soda and the frothers (xanthate and pine oil), the results seem to be slightly better than if the copper sulfate is added directly. Under these conditions the time of contact with the copper sulfate is only the short interval of time occupied in the pumping (by Wilfley pump) of the conditioned pulp to the zinc roughers.

It should be noted that the make-up soda is added, not in the grinding, but in the conditioning tank, the return circuit water being sufficiently alkaline for the lead float.

In order to account for the high tailing assay (in sulfide zinc) the idea presented itself that while there is undoubtedly oxide of zinc in the ore, the blende crystals, or some of them, even after grinding to the degree mentioned, might be enveloped in

films of oxide, which would, if not prevent, at least retard the good work of the copper sulfate in conditioning. It is, of course, well known that ammonium hydrate or carbonate are powerful solvents of zinc oxides. It was decided, therefore, to try and clean up the blende crystals by the addition of ammonia to the conditioning circuit. In the laboratory this has produced spectacular results.

Whereas previously the froths produced were rather thin and the flotation slow, the addition of ammonia produced much denser froths of very nice bronzy colored blende. The idea has not yet been given a proper tryout on a large scale in the mill.

The point at which the ammonia is added in the conditioning seems to be an important one. If the ammonia is added at the same time as the copper sulfate, no particular improvement is noticed over ordinary conditioning without ammonia. If it is added after the copper sulfate, the results are even worse; but if it is added before the copper sulfate, the results are good—better than in ordinary mill practice.

The best combination seems to be: Agitation for 10 min. with ammonia and the frothers (xanthate and pine oil) followed by 5 min. agitation with copper sulfate. If the frothers are added after the copper sulfate, *i. e.*, just before flotation, results are not so good.

The short contact with the copper sulfate is noteworthy. The alkalinity of the circuit before adding the ammonia is an important factor. It is thought that the ammonia may perform other functions than that of merely cleaning the faces of the blende crystals. Ammonia is, of course, a solvent for copper carbonates produced in the alkaline circuit. If free ammonia or ammonium carbonate are present in the circuit, there can be no doubt that the copper will remain in solution ready for reaction with the blende (unless it is precipitated as xanthate of copper, which appears to be insoluble in solutions of ammonia).

I doubt whether basic carbonates of copper are sufficiently soluble in the mill circuit water. They may form "colloidal solutions." I should imagine, however, that chemical reaction between a colloid and a solid would be slower than between a true solution and a solid.

The ammonia may also act as a dispersion agent in a beneficial manner to the flotation of the blende.

As strong ammonia is not pleasant stuff to handle in bulk, it was thought that perhaps a fixed salt (sulfate, chloride, nitrate, etc.) would act in the same manner if sufficient soda were added at the same time to actually liberate ammonia (or carbonate) in the circuit. Although the froths produced by the use of these salts were of the same kind as with ammonia, the tailings were not so clean. The concentrates produced, however, were of higher grade.

By making settling tests of the tailing produced by the use of salts of ammonia, it was found that the slime was highly coagulated, whereas with ammonia it was well dispersed.

Ammonium bicarbonate did not produce such good results as the hydrate.

I wish to thank the authors for their interesting papers and would like to ask if they have done any work with the use of ammonia or cuproammonium salts in activating blende, or if they are aware of such work having been done.

O. C. Ralston (written discussion).—Mr. Macfee's experience in the use of ammonium salts in connection with copper salts as activators is interesting. He asks if we have had experience along this line. One of the papers mentions the use of cuprous chloride dissolved in ammonia. In that case we used the ammonia as a means of producing a soluble copper compound, which could be introduced into an alkaline pulp. As noted in Fig. 2 (p. 404), a rougher concentrate produced under these conditions tends to be lower in grade than when copper sulfate is introduced directly into a lime pulp.

Copper hydrate is not usually regarded as a soluble salt but it is far from being an insoluble salt and its solubility in distilled water is measured by the conductivity imparted to the water. This is the common way of measuring solubility of slightly soluble compounds.

Even chalcocite will dissolve in lime water rapidly enough to activate sphalerite. We can obtain differential flotation of chalcopyrite away from unactivated sphalerite but the presence of chalcocite causes activation of the sphalerite to the same floatability as the chalcopyrite and prevents differential separation. With chalcocite, the explanation probably lies in its ease of oxidation, which forms the more soluble hydrate.

H. W. Hardinge, New York, N. Y.—There have been many cases where a man can get by his process more than can be obtained by assay and not by the well known "salting" methods either. I did that unknowingly by the use of differential flotation. In 1903, I was operating a mill at Massey, Ontario, where we used original bulk flotation; namely, the Elmore bulk flotation process. We separated the oil from the concentrates by the use of a centrifugal separator. The original ore contained about 2.5 per cent. copper. Concentration ratio was about 7/1, as there was a large percentage of iron in the ore. On this basis we should have obtained between 17 and 18 per cent. copper in the concentrate on the basis of 100 per cent. extraction. We shipped carload after carload that actually ran 22 per cent. in copper. Apparently I gained 125 per cent. of the values. If anybody can do better than that, let them go ahead and trot it out.

I did not know at that time that I was practicing differential flotation, although I did know how to account for the discrepancy after it developed. It is one of the interesting things that will often come up, where, as I say, we get more than 100 per cent. of extraction, but it was through what has been developed that we have differential flotation as explained here today.

C. E. Locke, Cambridge, Mass.—In the south, Ralston, and in the north, Gaudin, now are really translating flotation; they are making it intelligible to us who have not come up in the realms of physical chemistry and electrochemistry and so forth. I will confess frankly that I was lost in the old maze of flotation theory; in fact, I think Mr. Ralston himself has presented us with some of the older flotation theory, but now we are getting down to an intelligible basis for knowing what flotation is. It is developing a new realm of chemistry, minute chemistry. Flotation reagents today are perhaps in the order of 0.1 lb. per ton of ore. That is one part in 20,000, and as the dilution is often 5/1 it means that we have to deal with a chemistry of one part in 100,000. That is beyond the ken of ordinary quantitative determination.

Mr. Ralston has spoken about invisible films. What we have to do, I suppose, is to get a magnifier that will enable us to see those films, but the work which he has done is to make the whole thing understandable. We can understand how these chemical reactions are taking place, how the copper sulfate reacts; and it merely comes down to our old simple chemistry of just getting reactions to coat or uncoat, dress or undress, if you please, the mineral particles so that they will rise or fall exactly as we want them.

R. Gahl, Berkeley, Calif.—The development of the flotation process in a theoretical way has so far been confined to the universities and colleges. We all know about the splendid work done by the University of Utah, by Columbia University and by the Massachusetts Institute of Technology along those lines, but the encouraging feature of these papers is that now a mining company is coming into the field and contributing theoretical ideas on this obscure subject. I think we all should value greatly the contribution which the United Verde Copper Co. is making in that direction.

C. E. Locke.—Is there anybody here who remembers the work that Dr. Gahl of the Inspiration Copper Co. did some years ago, when he says that all of this work was done by the universities? I beg to remind him that that is not strictly true.

What is the future of this chemistry in connection with flotation? Do you feel that we are going to progress along that line, Mr. Ralston?

O. C. Ralston.—I feel that there are many obscure phenomena in flotation which have been stumbled upon by what Mr. Coghill describes as the method of "blundering empiricism."

The particular piece of work described in the two papers under discussion was designed to give a closer understanding and thereby a closer control of activators for sphalerite. We may accomplish no more than has been done in the past but we will do it more intelligently and probably more economically by the understanding of what we are doing.

Some of the remarks on what the Research Department of the United Verde Copper Co. is doing cause me to say that these papers are by-products of a commercial research with a definite commercial object, sufficiently carefully designed so that the results would have scientific as well as commercial value. Most industrial research can be carried out methodically in that way, although such an inspirational genius as T. A. Edison stands for trying out every conceivable thing in a more or less haphazard fashion. Careful thought and planning, with hypothesis at the basis of it all, even though the desired result is a commercial one, will bring results that are really of value theoretically.

This does not represent the work of many months or years, Professor Locke, but only two or three months' work on the part of two or three men. The first paper contains results of two months' work by one man and the second paper a similar amount of time by two men. Incidentally, we discovered how to treat our ore, which had previously been a difficult one; or, as we say in the Southwest, a "maverick."

# Effect of Xanthates, Copper Sulfate and Cyanides on Flotation of Sphalerite

By A. M. Gaudin,* Butte, Mont.

(Spokane Meeting, October, 1929)

Of the various reagents employed in the flotation of zinc-bearing ores none have attained the wide popularity that is enjoyed at present by xanthates, copper sulfate and cyanides. This situation suggests the existence of an unusual dependence in the reactions of these chemicals and of sphalerite. A study of the flotative characteristics of sphalerite when using xanthates as collectors, as related to the chemical properties of copper salts and cyanides, has therefore been conducted at the University of Utah by the writer and his associates[1] during the period of 1926 to 1929.

In perusing the technical literature concerning the flotation of zinc ores and of zinc-bearing lead and copper ores, a striking and general lack of agreement as to the floatability of sphalerite was observed. The underlying cause for the erratic behavior of sphalerite has not been definitely ascertained but the presence in various proportions of iron sulfide in solid solution in the sphalerite has frequently been implicitly regarded as a major factor in this respect. Although the effect of iron sulfide in solid solution in sphalerite has not been investigated in relation to the behavior of sphalerite in flotation, it is likely that it is not as important a factor as was thought at one time. The variable floatability of sphalerite has led to the use of fairly large amounts of cyanide to prevent its flotation in the case of certain ores, whereas mere fractions of that amount of cyanide, or even none at all, have been sufficient to achieve the same result for other ores.[2] Similarly, the amount of copper sulfate used to promote the flotation of sphalerite has been found to vary widely.

## Effect of Copper Salts in Distilled Water on Sphalerite

In the work at the University of Utah, over a year was spent in futile attempts at duplicating experiments until it was discovered that the

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* Research Professor of Ore Dressing, Montana School of Mines.

[1] A. M. Gaudin, C. B. Haynes and E. C. Haas: Flotation Fundamentals, IV. Utah Eng. Expt. Sta. *Tech. Paper* 9.

[2] A. W. Fahrenwald: Flotation Practice in the Coeur d'Alene District, Idaho. Flotation Practice, A. I. M. E. (1928) 122. See Table 9.

distilled water in use contained copper salts in amount large enough to affect the floatability of sphalerite yet small enough to remain undetected by ordinary analysis. The copper was picked up by the distilled water in course of storage in a tin-lined copper tank whose lining had worn in places, and it occurred to a concentration varying from 0.1 to 1.5 part per million. As soon as experiments were conducted with copper-free distilled water made from the distillation in a pyrex flask of alkaline water containing potassium permanganate and collected in glass, the concordance between duplicate experiments became satisfactory.

In connection with the finding that distilled water had to be absolutely copper-free to be used in testing the floatability of sphalerite, it was

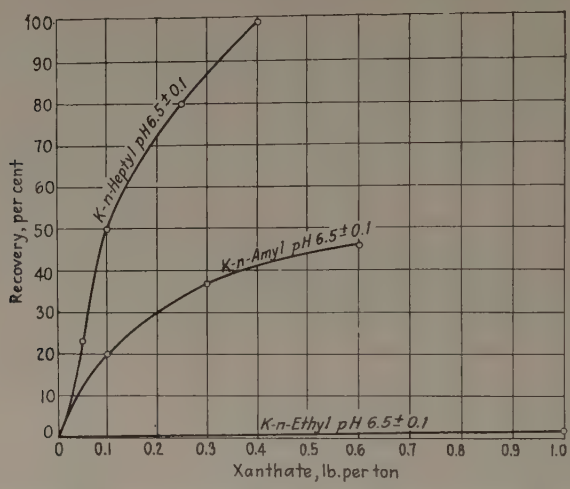


FIG. 1.—FLOATABILITY OF SPHALERITE WITH AMYL XANTHATE AND ETHYL XANTHATE.

established that washing sphalerite with 20 times its weight of distilled water containing copper to the extent of 0.1 part per million more than doubled the recovery of copper-free sphalerite with potassium ethyl xanthate. That activation of the mineral should follow the addition of such a minute amount of a copper salt is very remarkable from a chemical standpoint. It is highly suggestive, also, from a practical standpoint, inasmuch as very few zinc ores are so entirely free of copper as to preclude the presence of sufficient oxidized copper salts to produce some activation. If the hypothesis that all sphalerite is more or less activated by the copper salts that occur with it in nature is true, the variations in results reported in floating zincky ores would immediately be explained, both in what concerns the effect of xanthate alone, and in what concerns the desirable amount of cyanide to prevent the flotation of the sphalerite and of copper sulfate to promote it.

## Floatability with Xanthates

To establish the exact floatability of sphalerite with ethyl xanthate, experiments were conducted on an especially copper-free coarsely crystalline sphalerite which had been deslimed in copper-free water (Table 1). Under those circumstances the floatability of sphalerite was found to be substantially nil, even if large amounts of xanthate had been used. In fact, the floatability of pure sphalerite with ethyl xanthate is less than that of cerussite or that of malachite (if determined in the absence of these oxidized minerals so that salts from their surface cannot activate the sphalerite). The floatability of sphalerite when using amyl xanthate as the collector is small, although it is larger than with ethyl xanthate (Fig. 1) in accordance with Traube's rule[3] of which the applicability to flotation has already been indicated.[4]

Table 1.—*Analyses of Sphalerite*[a]

| Chemical Analysis | | Sizing Analysis after Desliming | | |
|---|---|---|---|---|
| Element | Per Cent. | Microns | Mesh | Weight, Per Cent. |
| Zn | 64.7 | −208 + 147 | − 65 + 100 | 2.4 |
| S | 31.6 | −147 + 104 | −100 + 150 | 21.1 |
| Fe | 1.1 | −104 + 74 | −150 + 200 | 22.3 |
| CaO | 0.15 | − 74 + 52 | −200 + 280 | 20.2 |
| Insol | 0.55 | − 52 + 37 | −280 + 400 | 16.5 |
| Cu | None | − 37 + 26 | −400 + 560 | 12.1 |
| Pb | None | − 26 + 18 | −560 + 800 | 3.9 |
| | | − 18 | −800 | 1.5[b] |

[a] Reproduced from Flotation Fundamentals, IV. (See footnote 1.)
[b] By difference.

The nonflotation of pure sphalerite when using ethyl xanthate as collector is in agreement with the substantial lack of abstraction of xanthate from solution by the mineral. (See Table 4.)

## Action of Copper Salts on Sphalerite

From a geological standpoint, the action of copper sulfate and of similar salts on sphalerite has long been known, some experiments having been reported as far back as 1911, by Rogers,[5] who found that visible blue-black coatings formed on sphalerite upon prolonged treatment with strong, hot copper sulfate solutions. Rogers' experiments were repeated

[3] H. Freundlich: Colloid and Capillary Chemistry. New York, 1926. Dutton.
[4] A. M. Gaudin: Flotation Fundamentals, I. Utah Eng. Expt. Sta. *Tech. Paper* 1.
[5] A. F. Rogers: Columbia School of Mines *Quarterly* (1911) **32,** 298; quoted in Clarke's Data of Geochemistry, 5th Ed.; U. S. Geol. Survey *Bull.* 770.

and the same results obtained, Fig. 2 being a photograph of one of the coatings so obtained.

The presence of copper in the coating was established by a microchemical analysis of spalls from the mineral surface and by qualitative tests on the liquor obtained by leaching the coated sphalerite with a strong cyanide solution. Little doubt remained that the coating was a copper sulfide—a conclusion already reached by Rogers and by Gates and Jacobsen.[6] Lack of reaction between the coating and a silver nitrate solution further showed the coating to be covellite, CuS, which is in complete accord with the reaction:

$$ZnS + Cu^{++} \rightleftarrows CuS + Zn^{++} \qquad [1]$$

Reaction 1 is of the double decomposition type and should proceed from left to right since the solubility product of zinc sulfide is acknowledged to be larger than that of cupric sulfide:[7]

$$[Zn^{++}][S^{--}] > [Cu^{++}][S^{--}] \qquad [2]$$

The activation of sphalerite by copper sulfate in very small concentration is also in agreement with the fact that the solubility product of cupric sulfide is extremely small compared to that of zinc sulfide.

## Rate of Reaction of Copper Salts with Sphalerite

Several attempts were made at measuring the rate at which reaction 1 proceeds. Table 2 summarizes the results obtained and brings out the

Table 2.—*Rate of Reaction*[a] *of Copper Nitrate with Sphalerite*

Milligrams of Copper Nitrate Abstracted by 25 Grams of Sphalerite Having a Surface of about 650 Square Centimeters per Gram from 25 Cubic Centimeters of Solution

| Copper Nitrate in Contact with the Mineral, Mg. | Time of Contact | |
|---|---|---|
| | 15 Minutes | 30 Minutes |
| 6.25 | 6.25 | —— |
| 12.5 | 8.8 | 12.3 |
| 25.0 | 10.0 | —— |
| 62.5 | —— | 13.7 |
| 75.0 | 12.0 | —— |
| 312.5 | —— | 16.7 |
| 1562.5 | —— | 20.25 |

[a] Reproduced from Flotation Fundamentals, IV. (See footnote 1.)

interesting fact that removal of an amount of copper sufficient to form a thin coating of covellite takes place rapidly, but that a considerable

[6] Thesis, University of Utah (1925).

[7] F. P. Treadwell (Translation by W. T. Hall): Analytical Chemistry, **1**, Qualiative analysis. 4th Ed. J. Wiley & Sons, New York.

increase in the time of contact or in the concentration of the solution is necessary to bring about a substantial thickening of the coating. The rapid formation of the coating on sphalerite by a copper sulfate solution—which is slightly acid—is no evidence, of course, that the same occurs in alkaline circuits in which the copper salt is precipitated as a carbonate, a hydroxide or a basic carbonate. But it should be mentioned that sphalerite conditioned for some time with malachite grains is considerably activated, no doubt because of solution of the copper from the malachite and migration of the copper ions to the sphalerite surface; the same effect is obtained in the case of sphalerite treated in alkaline pulp with a copper salt, and the explanation is no doubt the same. The only difference between treatment in a copper sulfate (acid) pulp and copper sulfate pulp made alkaline lies in the concentration of the cupric ion which is active. This concentration decreases as the alkalinity of the solution increases, so that a longer condition time is necessary in alkaline circuits.

The fact that the covellite coating at the surface of the sphalerite forms slowly in the later stages (which involve a diffusion in the solid state or a partial loosening of the coating with infiltrations of the solution below the coating) gives grounds for believing that a coating one atom thick must be substantially completed before the second atomic layer begins to form. Thus, the mental picture of sphalerite painted by covellite to the depth of one atomic diameter behaving as covellite rather than sphalerite is not a dream but a probability of high order.

The use of cyanide in preventing sphalerite from floating in lead or copper circuits of complex ores has become established as standard practice, and from the start it has been assumed—and even demonstrated[8]—that cyanide "sickened" or "deadened" sphalerite by modifying its surface. The joint use, in practice, of cyanide and zinc sulfate, and the fact that a comparatively insoluble zinc cyanide forms in concentrated solutions befogged somewhat actual the effects of each of these reagents.

## Cyanides Do Not Inhibit Unactivated Sphalerite

It has already been pointed out that ethyl xanthates do not collect sphalerite. In order to test the alleged depressing action of cyanides, it became necessary to use collectors other than the ethyl xanthates. Neither with amyl xanthate, thiocresol nor amyl mercaptan, all of which collect sphalerite to some extent, was any depression of the mineral obtained upon addition of cyanides—even if large amounts were used—

[8] E. L. Tucker and R. E. Head: Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals. *Trans.* A. I. M. E. (1926) **73,** 354. See also A. F. Taggart, T. C. Taylor and C. R. Ince: Experiments with Flotation Reagents. Pages 320 to 323, this volume.

proper allowance being made, of course, for the change in pH brought about by hydrolysis of the added cyanide:

$$CN^- + H_2O \rightleftarrows HCN + OH^- \qquad [3]$$

The negative character of the tests designed to bring out the depressing properties of cyanides on sphalerite made it appear unlikely that coatings should form on sphalerite as a result of treatment in a cyanide solution. It suggested also that little or no abstraction of cyanide should follow treatment of a cyanide solution with sphalerite. In agreement with Taggart, Taylor and Ince,[9] no coatings were observed. Abstraction tests resulted in a very small consumption of cyanide and in the solution of minor amounts of zinc. Thus, far from forming coatings on the surface of sphalerite, cyanides seem to dissolve it to a slight degree.[10] Such a chemical behavior is in agreement with the flotation result that cyanides do not depress pure sphalerite.

## Deactivation by Cyanides of Copper-activated Sphalerite

The behavior of copper-activated sphalerite upon treatment by a cyanide solution is very different from that of pure sphalerite, both from a flotative standpoint and from a chemical standpoint. Table 3 shows that cyanide deactivates sphalerite previously activated by copper sulfate, and points to the importance of the relations between cyanide ion, cupric ion and copper sulfides in explanation of the action of copper sulfate and cyanides on sphalerite.

Table 3.—*Deactivation of Sphalerite Previously Activated by Copper Sulfate*[a]

Amount of Reagents, Pounds per Ton

| Terpineol | Potassium Ethyl Xanthate | Sodium Cyanide | Copper Sulfate | Recovery, Per Cent. |
|---|---|---|---|---|
| 0.20 | 0.50 | | | 0 |
| 0.20 | 0.50 | | 0.1 | 100 |
| 0.20 | 0.50 | 1.0 | 0.1 | 0 |

[a] Reproduced from Flotation Fundamentals, IV. (See footnote 1.)

Copper forms two slightly soluble cyanides:[11] a cupric and a cuprous cyanide. Cuprous cyanide is more stable and forms from the former by elimination of cyanogen, the reaction being:

$$Cu(CN)_2 \rightleftarrows CuCN + \tfrac{1}{2}(CN)_2 \text{ or} \qquad [4]$$

$$Cu^{++} + CN^- \rightleftarrows \tfrac{1}{2}(CN)_2 + Cu^+ \qquad [5]$$

[9] *Loc. cit.*

[10] E. S. Leaver and J. A. Woolf: *Rept. of Investigations*, U. S. Bureau of Mines, Ser. 2883 (July, 1928). Also, Effect of Copper and Zinc in Cyanidation with Sulfide-acid Precipitation, this volume. See Table 9, page 536.

[11] J. W. Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Longmans, Green & Co. New York, 1922–29.

Cuprous cyanide is readily soluble in excess cyanide, forming a complex ion whose exact formula has recently been established by W. D. Bonner[12] and his associates as $Cu(CN)_3^{--}$. This cuprocyanide ion is slightly dissociated, the ratio $Cu(CN)_3^{--}$: $Cu^+$ in a solution about 0.01 N in copper and 0.03 N in cyanide being of the order of $10^{+30}$. In the presence of excess cyanide the ratio is larger still, so that the free cuprous ion and the free cupric ion are practically incapable of existence in cyanide solutions. Such minutely soluble copper salts as copper sulfides are therefore dissolved by cyanide, even though their rate of solution is small when they occur as coarse particles having little surface. The cyanicide properties of copper sulfide in the cyanide treatment of gold and silver ores[13] afford a practical example of the behavior of copper sulfides in cyanide flotation pulps.

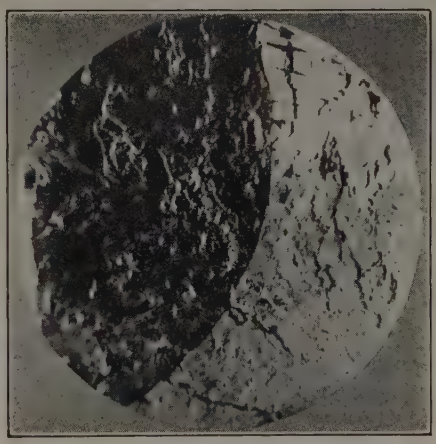

FIG. 2.—SPHALERITE COATED WITH COVELLITE (LEFT) AS THE RESULT OF TREATMENT WITH COPPER SULFATE.

Evidence of the decopperizing action of cyanide on covellite-plated sphalerite is found in Fig. 2, in which the light colored area represents the cyanide-leached covellite-plated sphalerite restored to its original sphalerite condition, and the dark colored area the covellite-plated sphalerite which has been protected from the cyanide solution by a temporary coating of collodion.

Abstraction and quantitative leaching tests on copperized sphalerite showed that cyanide abstraction is much larger than in the case of pure sphalerite and that substantially all the copper acquired by the sphalerite during the copperizing treatment is given up to a slight excess of cyanide.

Xanthate abstraction tests similar to those run with pure sphalerite were made with covellite-plated sphalerite, cyanide-leached covellite-plated sphalerite, and with cyanide-leached sphalerite. The abstraction of the xanthate expressed as a percentage of the total xanthate (0.2 lb. per ton) added are given in Table 4, which supports definitely the flotation results presented in Table 3.

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[12] W. D. Bonner: Private communication; also Master's thesis by S. Ravitz, Dept. Chemistry, Univ. Utah (1928).

[13] A. C. Halferdahl: Treating Cupriferous Precious Metal Ores by the Cyanide Process. *Eng. & Min. Jnl.* (Aug. 31, 1929). This article also contains an excellent bibliography.

TABLE 4.—*Abstraction of Xanthate Expressed as Percentage of Total Xanthate*

| Copper Sulfate Treatment, Lb. per Ton | Cyanide Treatment, Lb. per Ton | Abstraction of Xanthate, Per Cent. |
|---|---|---|
| —— | —— | 7 |
| 0.25 | —— | 98 |
| 0.25 | 1.0 | 6 |
| —— | 1.0 | 6 |

## CONCLUSIONS

In view of the evidence presented in this paper, the following conclusions appear justified:

1. Pure sphalerite does not abstract ethyl xanthate from solution and is not floated thereby.

2. Pure sphalerite reacts slightly with cyanide solutions; such reaction as occurs forms no coating on the sphalerite but leads to the solution of some zinc probably as a complex zinc-cyanide ion. Pure sphalerite is not depressed by cyanide.

3. Sphalerite readily acquires from copper-bearing solutions a coating of covellite having a thickness of a few atomic diameters; thereafter the reaction is slow. However, visible coatings of covellite can be prepared in the laboratory and identified as such.

4. Covellite-plated sphalerite abstracts xanthate from solution and is floated thereby.

5. The covellite coating of sphalerite previously treated with copper sulfate is readily dissolved by cyanide solutions owing to the formation of the substantially undissociated cuprocyanide ion. Cyanide solutions therefore have a cleansing effect on covellite-plated sphalerite surfaces.

6. Cyanide solutions greatly decrease the floatability of copper-activated sphalerite, bringing it back to the normal floatability of pure sphalerite, which is very slight with ethyl xanthates.

7. Natural sulfide zinc ores probably contain sphalerite in various stages of activation by copper salts and therefore call for the use of various amounts of cyanide and of copper sulfate in selective flotation.

8. Differences in the flotative properties of various native sphalerites are probably less dependent upon the iron content of the sphalerites, that is, their marmatitic character, than they are upon the natural activation by base-metal salts, particularly copper salts.

## ACKNOWLEDGMENTS

The author is indebted to Dr. D. A. Lyon, of the Department of Metallurgical Research of the University of Utah, for permission to use some material from *Technical Paper* No. 9 of the Utah Engineering Experi-

ment Station prior to the publication of that paper and to his collaborators at the University of Utah, E. C. Haas and C. B. Haynes. He also wishes to record his appreciation to President Francis A. Thomson, of the Montana School of Mines, for his suggestions and his constructive criticism.

## DISCUSSION

A. W. Fahrenwald, Moscow, Idaho.—I have not had sufficient time to put the amount of thought on Professor Gaudin's paper that it deserves.

A few days ago I read a paper written by Oliver C. Ralston and his associates at the United Verde, which brought up some of the same problems that Professor Gaudin has presented in his paper and I think came to similar conclusions on some of the points, particularly in regard to the chemical nature of the coating on the sphalerite.[14]

Speculation as to the nature of conditions at solid-solution contacts always is interesting. In the case of zinc sulfide (sphalerite) a question that interests me is the possible "fit" of the copper atom on the sulfide surface as it displaces the zinc atom of the sphalerite. What are the relative sizes or electronic make-ups of ionized copper and zinc atoms?

Does xanthate react the same with the artificial covellite coating produced by the action of copper sulfate on sphalerite as with the covellite of nature?

A. M. Gaudin.—Dean Fahrenwald has raised several interesting questions relating to the fine structure of the covellite coating forming on sphalerite from treatment of the mineral with copper salts. I do not know whether the covellite in the coating is identical to the natural covellite of copper ores. Under a binocular microscope the coating appears as a very soft, waxy, deep blue crust easily scratched with a steel point. The coating does not have any obvious macrocrystalline structure.

Sphalerite and covellite have slightly different specific gravities (approximately 4.0 and 4.6) but nearly the same molecular weights (approximately 97.4 and 95.4 respectively). The atomic spacing is therefore somewhat different. I do not know whether the difference in the atomic spacing is sufficiently large to preclude the replacement of zinc atoms by copper atoms, atom for atom. I am inclined to think that this replacement is possible for monatomic or very thin polyatomic films, but that it becomes difficult in the case of thick crusts.

Experimentally the coating that copper sulfate causes at the surface of sphalerite appears difficult to wear off. It is possible, of course, that it does wear off in one place but starts again at another point.

The coating observed by Dean Fahrenwald upon treatment of sphalerite by silver nitrate has also been observed by Mr. Haynes, who worked with me at the University of Utah. By analogy with the case of copper, I have thought that this coating was silver sulfide. The rapidity of formation is much greater than in the case of the covellite coating, perhaps because $Ag_2S$ does not fit as well in place of ZnS as does CuS: this poor fit may cause the formation of a more porous film through which diffusion of the fluid and continuation of the reaction can proceed.

A. W. Fahrenwald.—Have X-ray diffraction patterns been made of powder scraped from the surface of sphalerite?

A. M. Gaudin.—No, that experiment was not done, yet it would perhaps be very conclusive.

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[14] See page 369.

A. W. Fahrenwald.—I think perhaps the most interesting thing that Professor Gaudin brought out is the fact that clean sphalerite in clean water is not floated by xanthates. That is remarkable but understandable. If Professor Gaudin has any information handy on the solubility of zinc xanthates, that would be interesting.

A. M. Gaudin.—I have no figures as to the solubility of zinc xanthates. My recollection is that the solubility of zinc ethyl xanthate is of the order of one to ten parts per ten thousand. This is much more than the solubility of the copper or lead ethyl xanthates, which are of the order of one part per million or less. Of course, zinc amyl xanthate is much less soluble than the ethyl xanthate. Using Traube's rule, the solubility of each xanthate in homologous series should be about one-third of the solubility of that xanthate of the series having one $CH_2$ group less. On that basis the solubility of zinc amyl xanthate would be $1/27$ that of the ethyl xanthate, and the solubility of zinc heptyl xanthate would be some 250 times less than that of the ethyl derivative. This brings the solubility of the higher zinc xanthates in line with that of the lower copper and lead xanthates.

The solubility of the ethyl xanthate of cadmium, which is the element below zinc in the periodic table, is about 20 times less than that of the zinc compound. Mercury is below cadmium in the periodic table; accordingly the solubility of its xanthates is lower than that of the corresponding cadmium xanthates.

F. A. Thomson, Butte, Mont.—This research reported by Professor Gaudin is a splendid illustration of the way in which progress has been made and is to be made in the future in flotation fundamentals because it represents the clarification of a much befogged issue. In other words, we have been proceeding in this matter of flotation of sphalerite upon an imperfect basis—getting the results but, apparently, not getting them from the causes which we thought explained them.

That is likely always to be true and by clarifying this issue, particularly in clarifying the action of cyanide in this matter of flotation of sphalerite, Professor Gaudin has rendered a real service and made a substantial step forward, and it is just in that direction that future progress, of necessity, must come.

This discussion of precipitation, whether of covellite or chalcocite or in any event of copper sulfide of some kind or other on the surface of the sphalerite, calls to my mind that in the Royal School of Mines in London some years ago the tradition was prevalent that John Percy, father of the literature of metallurgy in the English language, had made an experiment in which he placed some pyrite crystals in copper sulfate solutions of different concentrations, put these in half a dozen pickle bottles, labeled them carefully, as an experimenter should always do, watched his experiment for a few months or years, then shoved the bottles back in some cubby hole or shelf in his laboratory where the bottles became covered over with dust and were forgotten. In due course of time, 30 years later, death came to John Percy. His laboratory was cleaned up and these pickle bottles were dug out. Somebody was smart enough to clean off the labels and look at the description of the experiments—and on this pyrite was a chalcocite coating. John Percy's experiment was a success but the experimenter never learned of his discovery. It is an interesting story—not particularly germane to this discussion but worth keeping in mind.

W. L. Zeigler, Wallace, Idaho.—The outstanding feature in the use of flotation reagents is the small quantity actually required. Some years ago when froth flotation was first brought from Australia the chief reagents used were oelic and sulfuric acids, and if flotation was not complete we blamed the flotation machine rather than the reagents. The process then was not necessarily considered a chemical one or one depending upon chemical reactions.

In the last five years more progress has been made in the discovery of the fundamentals of flotation than had been accomplished in all the time before. This has been made possible by the discovery that the process is one depending upon chemical reactions. The use of copper sulfate, as I understand, which is so necessary to the flotation of sphalerite, was discovered in about 1914.[15] At that time bronze impellers were used in a flotation machine which was operating on an ore requiring an acid circuit. Naturally copper sulfate was produced in the circuit and the result was that sphalerite floated. In this way the use of copper sulfate was discovered accidentally, although very little was understood about the actual reactions that took place. It has been used ever since, and it is about the only flotation reagent of any importance that has never been patented and which all may use without charge.

E. Gayford, Salt Lake City, Utah.—To most of us, even in a meeting of metallurgists, this discussion between Professor Fahrenwald and Professor Gaudin savors a little of the Einstein theory of relativity. However, I think we all realize that the practical benefit that is bound to follow these supertechnical investigations is of immense benefit to the art.

Even as closely as I am compelled to follow such matters, I do not believe that I had read previously that pure sphalerite would not float—but it is only by starting with pure mineral that we find out how to handle the minerals as they occur in nature. One of the most important things, it seems to me, to find out is some other way than by "the rule of thumb" to know what quantity of these reagents to use in practice.

Take copper sulfate, even in the experimental stage, we start, say, with ¼ lb., see what that does, then go to ½ lb., then 1 lb., and in one case that I remember, we went to 3 lb. That kind of work is duplicated in a mill. The mill metallurgist looks over his test results and says, "Well, these fellows have been testing it; they got pretty good results with 1 lb. and I will start with 1½ lb." This gives him pretty good results and so, perhaps for months, he uses 1½ lb., whereas the condition with his return circuit, the mill water and various other factors would have allowed him to use considerably less.

If this class of supertechnical investigation will give the practical metallurgist some line he can follow whereby he will know very shortly how to get the benefit from the use of a minimum amount of reagents, we have made a tremendous stride.

Nothing has been said with reference to the use of cyanide as a depressant of iron in high alkaline circuits in the floating of iron-copper ores and I would like to know whether Professor Gaudin is working in that field extensively and whether he can tell us what cyanide does with such ores?

A. M. Gaudin.—I have no particular information concerning the effect of cyanides on copper-iron ores, as our experiments in that direction are entirely too embryonic to justify definite statements. The subject is most interesting as well as difficult of solution, and some time may elapse before a satisfactory understanding of the reactions of cyanides on copper-iron ores is attained. Our friends in the Research Department of the United Verde Copper Co., under the guidance of O. C. Ralston, have been doing some splendid work on the effect of lime on pyritic copper ores. It is to be hoped that they will follow this by similar work on the effect of cyanides.

Mr. Gayford mentions also the amount of copper sulfate used in zinc flotation. In connection with some work for the U. S. Bureau of Mines, I studied the records on the consumption of reagents in a number of plants in the United States. My recollection is that the amount of copper sulfate used per ton of ore is decreasing materially from year to year until it is less than one pound per ton of ore.

W. L. Zeigler.—Have you gone into the investigation of sphalerite with iron combined, such as marmatites, to see if this action is the same? Does the iron composition of the zinc affect the action?

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[15] See page 400.

A. M. Gaudin.—We have not studied in detail that phase of the work because we could not get dependable marmatite. Most of the marmatite that we secured was mixed with more or less pyrrhotite or pyrite. I do not expect great differences in behavior between marmatite and sphalerite, although marmatite might lean somewhat toward the behavior of pyrrhotite.

Many of the difficulties with marmatite may perhaps be traced to the fact that we are more exacting in connection with marmatitic ores. If a certain grade of zinc concentrate has to be maintained with an iron-bearing sphalerite, much better selection of the zinc mineral over associated pyrite or pyrrhotite has to be attained than in the case of a pure sphalerite.

W. L. Zeigler.—In the Coeur d'Alene our zinc minerals occur chiefly as marmatites, and, I believe, a whole series of these. In the Star, they point out marmatite with five distinct colors and each has relative floatability.

L. O. Howard, Pullman, Wash.—I think Mr. Ziegler's question is fully answered in the two papers by Ralston and his associates.[16]

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[16] See pages 389 and 401.

# Calculations in Ore Dressing

By W. Luyken* and E. Bierbrauer,* Düsseldorf, Germany

(New York Meeting, February, 1929)

A number of articles have been published, notably those by R. S. Handy, R. T. Hancock and A. P. Watt in *Engineering and Mining Journal*, dealing with the calculations involved in ore dressing. These publications demonstrate both the importance of the subject and the lack of success in developing a generally recognized method for comparing enrichment effects.

Considering that we may wish to compare enrichment results on similar or dissimilar ores, that we may desire to make the comparison on the basis of either the absolute or the economical efficiency, and that the number of factors upon which the result depends is large, the question arises whether it is possible to set up a positive method for such calculations. In the following pages it is our aim to show that a sure, complete and successful way to overcome existing difficulties has been found.

## Graphical Analysis of Ore-dressing Processes

The following is from Truscott's Text Book of Ore Dressing (London, 1923):

$x$ = assay of ore treated (feed).
$y$ = assay value of the concentrate.
$z$ = assay value of the tailing.
$a$ = weight of feed.
$b$ = weight of concentrate.
$c$ = weight of tailing.

$$C = \text{fractional concentration} = \frac{b}{a} = \frac{x - z}{y - z}. \tag{1}$$

$$K = \text{ratio of concentration} = \frac{1}{C} = \frac{a}{b} = \frac{y - z}{x - z}. \tag{2}$$

$$R = \text{fractional recovery} = \frac{yb}{xa} = \frac{Cy}{x}. \tag{3}$$

$100R$ = percentage recovery. $C_{\text{opt}}$ = theoretically best concentration. $100 - C_{\text{opt}}$ = waste in the feed.

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* Kaiser Wilhelm Institut für Eisenforschung.

In Fig. 1 the abscissas are concentration percentages and the ordinates assay percentages. The horizontal line $DC$ shows the assay of the feed and the area under $DC$ is the valuable content of the feed. The diagram further shows this quantity of valuable material divided by a dressing process into two products, *viz.:*

1. Concentrate (quantity = per cent. $C$; assay value = $y$).
2. Tailing (quantity = 100 − per cent. $C$; assay value = $z$).

The quantities of valuable content in these products are shown by the areas $AGFE$ and $EIHB$, respectively. The sum $y \times$ per cent. $C$ + (100 − per cent. $C$)$z$ is the original valuable content of the feed, and is, therefore, equal to $100x$. In other words, the rectangles $DKFG$ and $IHCK$ are of the same area. The diagram shows also the ideal case,

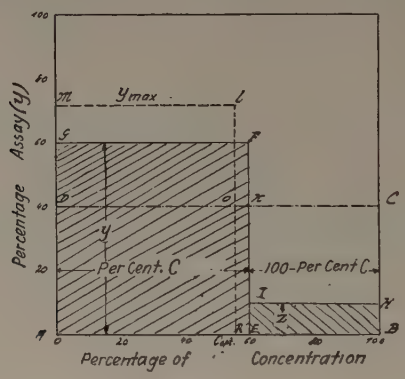


Fig. 1.

*i. e.*, separation into pure concentrate (value = $AMLR = y_{max}\ C_{opt}$) and pure tailing (value = $RB = (100 - C_{opt})\ 0 = 0$). Now, rectangle $DOLM = RBCO$.

This ideal shows the maximum enrichment that can be effected without chemical disintegration of the valuable mineral, and is a standard of comparison for judging the degrees of enrichment and the relative efficiencies of different processes.

The possible extent of enrichment increases and approaches the ideal as the structure of the ore becomes simpler and the physical properties of the different constituents of the ore diverge. The extent to which concentration depends upon the assay value of the concentrate cannot be shown by a simple rational formula, but can be calculated in due course empirically by a diagram embodying factors obtained by research.

Single concentrating machines and plants as a whole ordinarily produce a number of different products, which the ore-dresser classifies according to contained value as concentrate, middlings and tailing. Even if only two products are made, it is usually possible, by regulation

of the enrichment process, to change the assay values of the products. We come, then, to the question: Which of the possible degrees of concentration and what assay values are most desirable? This problem can be solved only by means of a diagram that shows how the assay value of the concentrate varies with the degree of concentration, *i. e.*, which graphs the relation $y = f\ (C)$. This relation thenceforth becomes the basis for numerical investigation as well as of technical progress and economical operation.

The first proposals to follow the course of ore-dressing operations by means of graphs were made in the coal industry, and the Belgian, Henry, was the first to make the application. His was probably the initial move toward systematic graphology in this field. The method is now

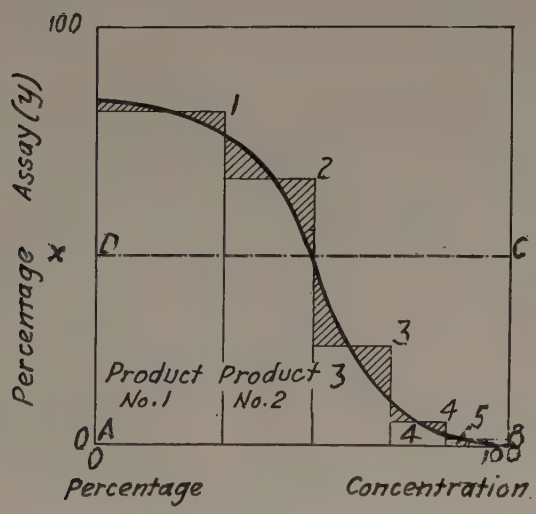


Fig. 2.

used widely in German coal-dressing and experiments indicate its utility in studying the treatment of metalliferous ores.

Fig. 2 sets forth the results of dressing a crude ore and dividing it into five products of declining assay value. The various products are plotted in order of decreasing assay value, according to the method employed in Fig. 1, so that the area of each block represents the weight of metal in the corresponding product, and the sum of these areas is the area *ADCB*, which is the weight of metal in the crude ore. The area under a continuous curve, drawn as shown, is substantially equal to the sum of the areas of the individual rectangles, the approximation being the closer, the greater the number of products. This curve forms the basis for analysis of the concentrating operation. Thus to determine

the assay of the concentrate for any given value of per cent. $C$, divide the area under the curve to the left of an ordinate erected at the given value of per cent. $C$ by this value of per cent. $C$. The required area may be determined by planimeter measurement or by approximate calculation.

By repetition of the above operation, with values of per cent. $C$ taken at sufficiently small intervals, a second curve is obtained (II, Fig. 3) which shows progressive assay values of the concentrate that can be made, if a particular percentage of the weight of the feed equal to the given value of per cent. $C$ is taken as concentrate. Curve III, Fig. 3, shows similar progressive assay values of the tailing for each value of per cent. $C$. It is obtained similarly to curve II, except that

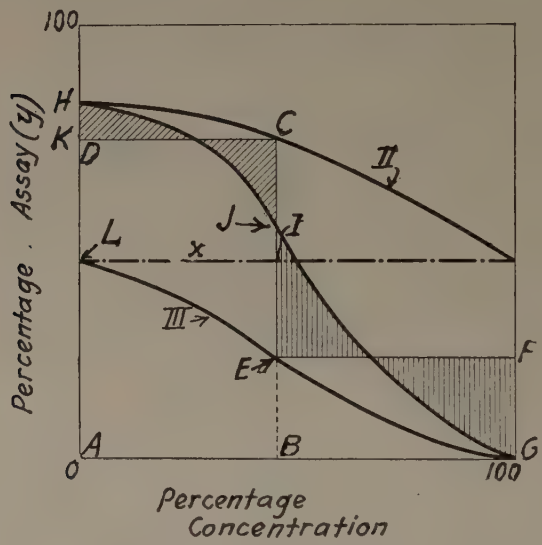


FIG. 3.—CHARACTERISTIC OF ENRICHMENT.

any given value of $y$ is determined by dividing the area under the curve to the *right* of any given value of per cent. $C$ by the corresponding value of 100 − per cent. $C$. It is apparent that point $C$ on curve II must *always* fall at the corner of the first rectangle, as shown, if curve I is so drawn that the area beneath it up to this value of per cent. $C$ is equal to the area of the rectangle. Similarly the terminal point of curve II must always fall at the intersection of line $x$ with the ordinate for 100 per cent. $C$. The initial point must always coincide with the initial point of curve $I$. In most cases only one or two points need be found between $C$ and the terminal point in order to permit smoothing in the curve. A similar method of approximate construction applies to curve III.

If $C_1$, $y_1$ and $C_2$, $y_2$ are concentration and assay values of two products that are to be mixed, for example two consecutive layers, and if $C = C_1 + C_2$ and $y$ the assay of the combined product,

$$Cy = C_1y_1 + C_2y_2, \text{ and}$$

$$y = \frac{C_1y_1 + C_2y_2}{C_1 + C_2}. \tag{4}$$

The "Characteristic of Enrichment," as Fig. 3 may be termed, shows, for any value of per cent. $C$, corresponding assays of concentrate and combined residue, for the particular concentrating operation under investigation.

It is apparent that, in Fig. 3, curve $I$ is of the nature of a differential curve, giving at any point for the particular concentrating operation therein illustrated, the assay value per unit weight of concentrate of that particular unit of weight, and of that only. In other words, the

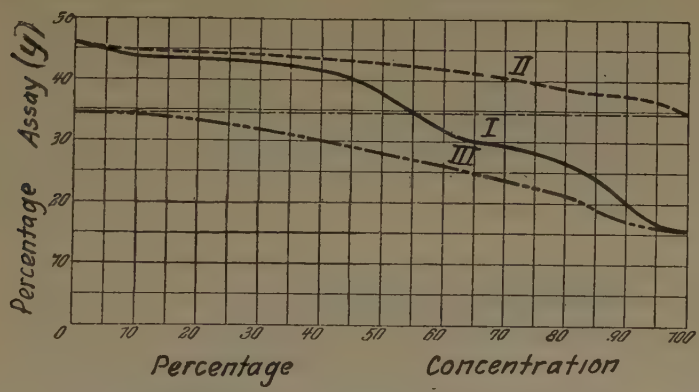


FIG. 4.—CHARACTERISTIC OF ENRICHMENT FOR A LOW-GRADE IRON ORE.

assay value of that unit weight of material that, as concentrate, represents the $AB$ per cent. of the feed removed, would have, according to Fig. 3, an assay value equal to $BJ$. The ordinates of curve II, on the other hand, represent average assay values, so that the value read at $C$, for example, is the average value of the entire $AB$ per cent. of concentrate removed up to this particular point in the operation. Mathematically, $BC$ is the mean ordinate of the area $AHJB$. Similarly, $BE$ (curve III) is the assay value of the tailing remaining when $AB$ per cent. of the feed has been taken out as concentrate, and mathematically $BE$ is the mean ordinate of the area $BJG$.

Fig. 4 is the characteristic of enrichment for a low-grade iron ore, difficult to concentrate. It was treated by washing, screening and jigging, making a number of products. Curve II shows that for a concentrate containing 43 per cent. Fe the percentage concentration is

40 (2.5 tons crude ore to 1 ton of concentrate), and that a concentrate assaying 40 per cent. Fe would have represented 75 per cent. of the original feed (ratio of concentration = 1.33). Curve III shows a tailing

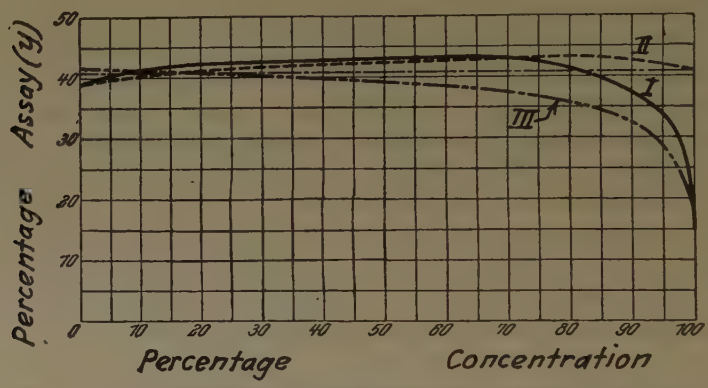


FIG. 5.—CHARACTERISTIC OF ENRICHMENT FOR A BROWN IRON ORE.

assay of 30 per cent. iron corresponding to the 43 per cent. concentrate, and 23 per cent. Fe to the 40 per cent. concentrate.

Fig. 5 is the characteristic for an experiment on a brown-clay iron ore which consisted chiefly of nodules and fragments embedded in clay. The most important grains were those 0.04 to 0.08 in. size, which

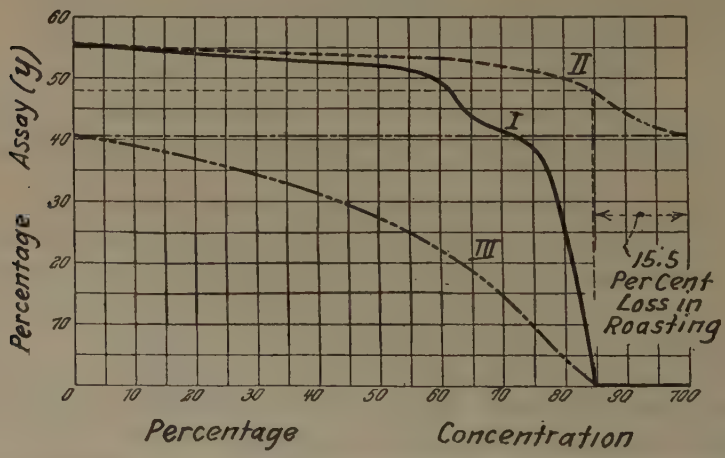


FIG. 6.—CHARACTERISTIC OF ENRICHMENT FOR THE ORE OF FIG. 5. AFTER ROASTING.

could be enriched only with great difficulty and the concentrate assayed only slightly higher than the tailing. Bulk concentration by magnets had been found unsatisfactory, but a number of single products were made with gradually increasing magnetic fields until only a small amount

of tailing remained. It was then seen, unexpectedly, that the first concentrate, *i. e.*, the most permeable, did not contain the most iron, but that the assay value of concentrate first rose slowly and thereafter declined. Fig. 5 shows that with a feed of about 41 per cent. Fe the first concentrate assayed less than 40 per cent. Fe, and that the best concentrate possible in this operation assayed only 43 per cent. Fe, corresponding to a value of per cent. $C = 65$ per cent. (about 1.5 tons into 1) and a tailing assaying 38 per cent. Fe.

Fig. 6 is the characteristic for an experiment with the same ore in which reducing roasting preceded magnetic separation. It shows that with a concentration of 60 per cent. ($1\frac{2}{3}$ into 1) the concentrate assay would be 53 per cent. Fe and the tailing about 22 per cent. Fe.

## Absolute Enrichment Effect

Enrichment operations may be compared either on the basis of their absolute or of their economic effect. It will be shown later which basis is more advantageous under various circumstances. Ordinarily the better absolute efficiency will correspond with the better economic efficiency.

Barring a few exceptional cases, the preceding method does not suffice for making comparisons between separating efficiencies. Hancock,[1] recognizing this, proposed a statement for metallurgical efficiency as follows:

$$\text{Percentage metallurgical efficiency} = \frac{100 \times \text{per cent. recovery} - \text{per cent. concentration}}{\text{per cent. waste in feed}}$$

The writers came to the same statement independently by means of the following reasoning. It is the object in ore dressing to attain a high recovery ($R$) and large ratio of concentration $\left(\frac{1}{C}\right)$. The difference $R - C$ is a measure of success. By setting $R - C$ as numerically representative of the enrichment actually attained and $1 - C_{opt}$ as representative of the enrichment theoretically possible, an efficiency index may be obtained from the equation

$$\eta_{abs} = \frac{R - C}{1 - C_{opt}} \tag{5}$$

In the denominator the numeral 1 represents complete recovery, *i. e.*, 100 per cent., and the concentration $C_{opt}$ is the percentage of valuable mineral in the feed. For example, in an ore containing 2 per cent. Pb as galena, $C_{opt} = \frac{2}{0.866} = 2.31$ per cent. Since $C_{opt}$ corresponds to the

[1] R. T. Hancock: The Economics of Ore Concentration. *Eng. & Min. Jnl.* (1918) **106**, 841.

weight of valuable mineral in the ore, $1 - C_{opt}$ equals the weight of gangue. Let Fig. 7 be taken to represent the enrichment characteristic for a given concentrating process on an ore assaying $OD$ $(= x)$, in which $OC$ $(= C)$ per cent. of the ore is taken as concentrate assaying $CG$ $(= y)$. Let $BE$ $(= y_{max})$ be the maximum possible assay of concentrate and $AB$ $(= C_{opt})$ be the maximum possible enrichment. Then rectangle $DLEF$ represents the maximum possible transfer of value from feed to concentrate. The enrichment actually obtained is shown by the shaded area and this is equal to the area of rectangle $DKGH$ as explained in connection with Figs. 2 and 3.

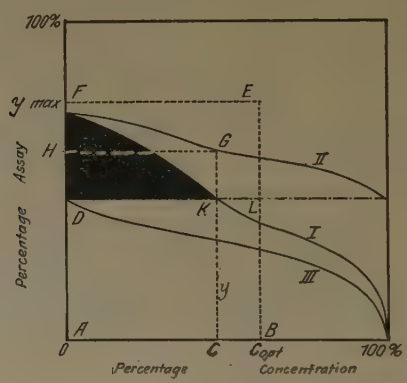


FIG. 7.

Then

$$\eta_{abs} = \frac{DKGH}{DLEF} = \frac{(y - x)C}{(y_{max} - x)C_{opt}} = \frac{yC - xC}{y_{max}C_{opt} - xC_{opt}}.$$

But

$$C_{opt}y_{max} - C_{opt}x = x(1 - C_{opt}),$$

hence

$$\eta_{abs} = \frac{yC}{x(1 - C_{opt})} - \frac{xC}{x(1 - C_{opt})},$$

and since

$$R = \frac{yC}{x}, \tag{6}$$

$$\eta_{abs} = \frac{R}{1 - C_{opt}} - \frac{C}{1 - C_{opt}} = \frac{R - C}{1 - C_{opt}}. \tag{7}$$

Of the numerous formulas that have been published, the writers believe that the one just developed, in the form

$$\eta_{abs} = \frac{C(y - x)}{C_{opt}(y_{max} - x)}, \tag{8}$$

is the most useful. It will be shown later that a statement for economic efficiency can be put into substantially the same form.

In prior publications dealing with absolute or metallurgical efficiency, one important point has been omitted, namely, consideration of the concentration or assay value of concentrate at which the efficiency attains its maximum value. Fig. 8 is based on treatment of an ore containing 30 per cent. metal. The mineral to be concentrated assays 70 per cent. metal ($y_{max} = 70$), hence the theoretically best concentration ($C_{opt}$) is:

$$30 \times {}^{100}/_{70} = 42.87 \text{ per cent.}$$

Curves I and II are plotted as in Fig. 3. The recovery curve $R$ graphs equation (6); the efficiency curve $\eta$, equation (8); the curve marked

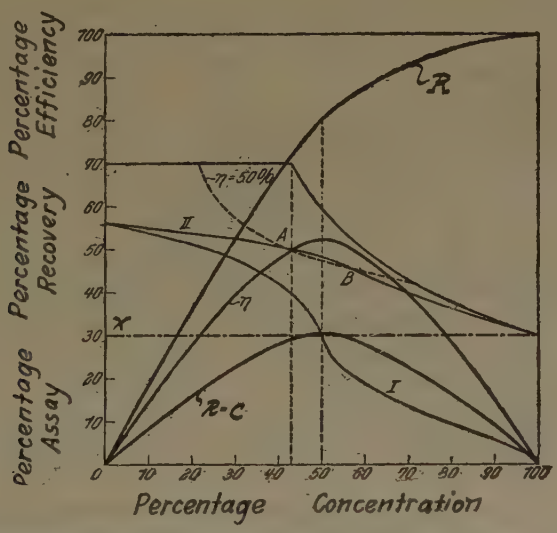


FIG. 8.—ENRICHMENT CHARACTERISTIC WITH CURVES SHOWING RECOVERY AND EFFICIENCY.

$R$-$C$ is plotted from ordinates derived by subtracting from the ordinate of the $R$-curve at that point the numerical value of the abscissa. The recovery curve rises rapidly up to about 80 per cent., after which the rise is more gradual. Note that this change in slope, which is rather indefinite, takes place at the same value for the concentration, *viz.*, 50 per cent., as that at which the curves for efficiency and $R$-$C$ reach their maxima. For all other degrees of concentration the efficiency is lower and a value for efficiency determined at random could only by chance illustrate truly the possibilities of the enrichment method employed.

Curve $R$-$C$ shows a maximum on the same ordinate as the efficiency curve. This follows from the relation expressed in equation (7).

The efficiency curve gives values that permit comparison between different operations independent of the assay of the ore treated. This

independence, which is the most important point about the efficiency curve, follows from the fact that the efficiency is a pure ratio between the actual enrichment effect and the maximum theoretically possible.

The efficiency curve shows that all values of efficiency between 0 and the maximum are attainable for two values of the concentration. Hancock[2] pointed this out and showed that the concentrate obtained between the two points of equal efficiency must be equal in assay to the assay of the feed. Fig. 8 shows a "curve of equal efficiencies" for the efficiency 50 per cent. (marked $\eta$ = 50 per cent.) This curve crosses curve II at points $A$ and $B$. The material which lies between the ordinates of

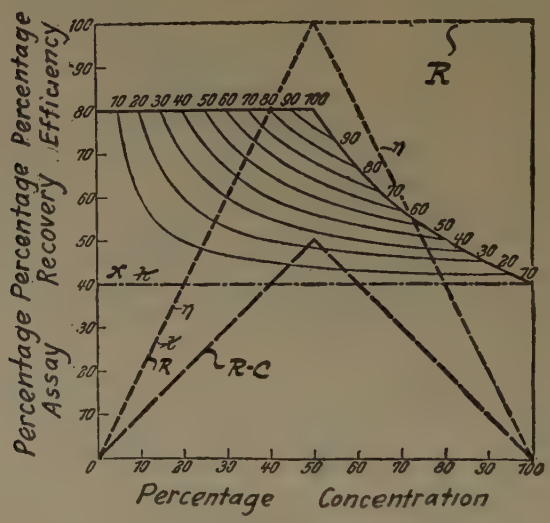


FIG. 9.—CURVES OF EQUAL EFFICIENCY.

$A$ and $B$ has the average assay value of 30 per cent. metal (see curve I). This follows from the fact that efficiency, by definition, is the ratio of actual enrichment to maximum possible enrichment, and, since the denominator of this fraction is a constant for any given ore, the numerators for equal values of the ratio must be the same. But equality of the numerators can exist only when transfer of material to concentrate results in no enrichment, *i. e.*, when the material transferred from feed to concentrate has the same assay as the feed.

Curves of equal efficiency may, under certain circumstances, be used to determine graphically the maximum efficiency. In Fig. 9 the basis

[2] R. T. Hancock: *Ibid.*

is an ore of 40 per cent. assay and the assay of pure valuable mineral ($y_{max}$) is 80 per cent. $C_{opt}$ is, therefore,

$$40 \times {}^{100}/_{80} = 50 \text{ per cent.}$$

Since positive values of efficiency can occur only when concentrate assays higher than the ore treated, the curves of equal efficiency must lie above line $x$, representing the feed assay. Zero efficiency lies along this line. The efficiency 100 per cent. is possible at one single point only, namely when pure mineral assaying 80 per cent. metal is separated in a concentrate weighing 50 per cent. of the original ore ($C = 50$). The curve for 30 per cent. efficiency must start where 30 per cent. of the valuable mineral has been separated in a concentrate assaying 80 per cent. ($C = 15$, $y = 80$); it must terminate at the point where all of the metal has been taken into the concentrate (100 per cent. recovery). The $C$, $y$ coordinates of this point are found by first placing $\eta = 30$, $R = 100$ and $C_{opt} = 50$ in equation (7), whence $C = 85$; then substituting this value of $C$ together with $40 = x$ and $80 = y_{max}$ in equation (8) and finding $y = 47$. Intermediate points on the 30 per cent. curve and points for the other curves are found similarly.

Fig. 9 shows values of the recovery ($R$), efficiency ($\eta$), and of $R$-$C$ for ideal enrichment of a 40 per cent. ore. $R$ and $\eta$ are coincident straight lines up to 100 per cent. at $C = 50$ per cent., which is the value of $C_{opt}$. As $C$ increases beyond $C_{opt}$, as a result of adding gangue to the concentrate, recovery remains constant at 100 per cent., efficiency falls on a straight line back to zero. Hence the maximum of technical enrichment is reached when 100 per cent. recovery is made in the form of a concentrate of pure valuable mineral.

When the performance of a particular machine is under investigation the absolute or metallurgical maximum efficiency discussed may be utilized to determine an efficiency figure for the machine itself. For example, in investigating a jig, if the maximum absolute efficiency on a certain ore is 60 per cent., but separation by heavy fluids gives an absolute efficiency of 75 per cent., the efficiency of the jig would be 60/75 = 80 per cent. The writers have named this the technical efficiency, and propose therefore the equation:

$$\eta_{techn} = \frac{\text{max. abs. efficiency of the actual separation}}{\text{max. abs. efficiency of a standard comparative process involving the same physical principle}}.$$

The writers consider this technical efficiency a novelty, since it gives a numerical statement of the degree of success of the machine with the effect of the natural properties of the ore eliminated. The technical efficiency is a measure of the extent to which a concentrating machine succeeds in utilizing the susceptibility to separation which the ore has owing

to its physical character. Absolute efficiency gives no clue to whether a low value is due to difficulties of separation inherent in the ore or to inaptitude of the machine in use. Nevertheless technical efficiency of a machine is dependent on the character of the ore treated. For instance, a jig fed with a mixture of galena and quartz may attain a technical efficiency of 99 per cent., whereas the same machine fed with a mixture of particles differing but slightly in specific gravity could not possibly reach so high an efficiency.

The method of absolute efficiency is applicable to analysis of performance in sizing. Thus, in the Dorr classifier consider the raw discharge concentrate and the overflow tailing. Let the percentages of oversize in feed, sand and overflow be considered the assay values, $x$, $y$ and $z$, respectively. Then, from equations (6, 7, 8), the absolute efficiency may be written:[3]

$$\eta = \frac{\text{recovery of oversize in the coarse material} - \text{concentration of coarse material}}{\text{undersize in the feed}}.$$

Since, in practice, the products are generally not weighed, the concentration and the recovery must be calculated by applying the results of the screen analyses, *i. e.*, from the values $x$, $y$ and $z$.[4]

## Economic Enrichment Effect

The basis of rational management of an ore-dressing plant is correct solution of the query: What grade of concentrate must be made, in light

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[3]
$$\eta = \frac{(y - x)C}{(y_{max} - x)C_{opt}}$$

But
$$C_{opt} = \frac{x}{y_{max}}, \quad y_{max} = 1, \text{ and } R = \frac{yC}{x} \qquad \text{[equation (6)]}$$

Substituting in equation (8)

$$\eta = \frac{R}{1 - x} - \frac{C}{1 - x} = \frac{R - C}{1 - x} \qquad (9)$$

(A. F. Taggart.)

[4] Substituting values in terms of assays for

$$R\left[= \frac{y(x - z)}{x(y - z)}\right] \text{ and } C\left[= \frac{x - z}{y - z}\right] \text{in equation (9)}$$

$$\eta = \frac{(y - x)(x - z)}{x(y - z)(1 - x)} \qquad (10)$$

which is the same as Dean's equation. See A. F. Taggart: Handbook of Ore Dressing, 1242. New York, 1927. John Wiley & Sons, Inc.

(A. F. Taggart.)

of the capability of the plant and the character of the ore, to obtain the maximum financial return?

The writers have already shown that the relation between concentration ($C$) and assay of concentrate ($y$) can be considered as a function, $y = f(C)$. The form of this function is a specific characteristic of any particular ore and enrichment process. Every change in ore character, either in assay value or in texture, and every change in the process used, causes a change in shape of the characteristic of enrichment. (Fig. 3.)

The function $y = f(C)$ can only be determined empirically. Set forth graphically, it forms the basis for systematic judgment of tests and of plant performance. But investigation of economic efficiency requires that, in addition to consideration of the maximum absolute efficiency, attention must also be paid to costs of production, existing prices and market possibilities. In any particular dressing process we can take either a small but highly valuable concentrate or a larger quantity of lower assay and correspondingly lower selling price. The weight and the unit value of the salable products are, therefore, dependent variables whose product, for a given constant mill feed, passes through a maximum. This point, which marks the best economic extraction, is characterized by a maximum total extraction profit up to the point of concentrate shipment.

Since mining calculations are ordinarily based on the ton of crude ore, the question of best economic enrichment may be phrased as follows: To what extent must a ton of crude ore be beneficiated in order to obtain the maximum profit per ton, assuming a definite flow sheet and, consequently, fixed dressing costs. Table 1 shows that maximum gain per ton of crude ore and maximum gain per ton of concentrate do not necessarily apply to the same operation.

TABLE 1.—*Profit per Ton of Concentrate and per Ton of Crude Ore*

| Feed, Tons | Weight of Concentrate, Tons | Selling Price per Ton of Concentrate | Total Amount Realized by Sale | Total Cost | Total Gain | Gain per Ton of Concentrate | Gain per Ton of Crude Ore |
|---|---|---|---|---|---|---|---|
| 100 | 50 | $20.00 | $1000.00 | $500.00 | $500.00 | $10.00 | $5.00 |
| 100 | 30 | 30.00 | 900.00 | 500.00 | 400.00 | 13.33 | 4.00 |

Fig. 10 is the enrichment characteristic for an ore which contains only one valuable mineral, with the per-ton selling prices of the various grades of concentrate marked thereon.

Since, in dressing 100 tons of crude ore, $C$ tons of concentrate are obtained, the amount realized from the sale of the concentrate produced from 1 ton of crude ore, signified by $E$, is $E = CV/100$, where $V$ is the selling price per ton of concentrate. Thus from curve $V$ (Fig. 10) curve $E$ (Fig. 11) is obtained. This shows the return per ton of crude ore for every degree of concentration.

In order to determine profit total expense must be considered. Since the basis of the enrichment characteristic is a given ore and given flow sheet (p. 438), the cost per ton of crude ore remains almost constant.

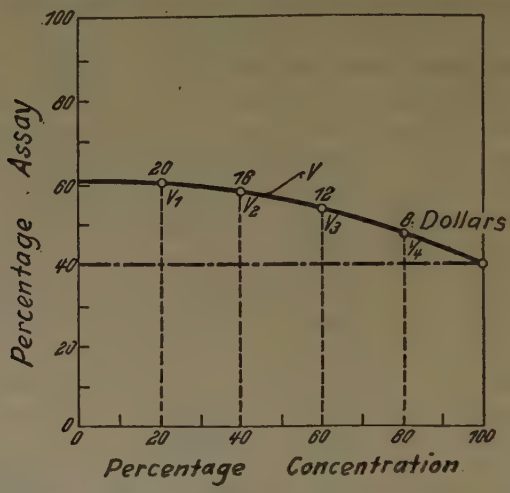


FIG. 10.—ENRICHMENT CHARACTERISTIC FOR ORE CONTAINING ONE VALUABLE MINERAL.

The various concentrate assays merely mark differences obtained by changing the performance of units in a plant unchanged as a whole. The opinion is commonly held that in order to obtain richer concentrate,

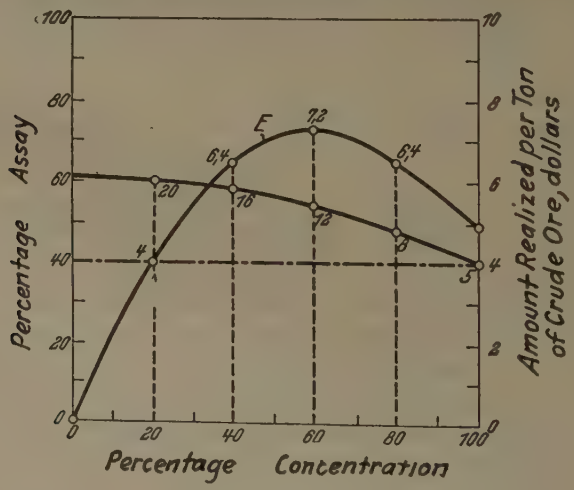


FIG. 11.—RETURN PER TON OF CRUDE ORE.

working costs must be higher. But this is not necessarily so. In magnetic separation, for example, the opposite may be the fact, since electric current for excitation is saved in reducing the strength of the magnetic

field in order to take a richer concentrate of higher magnetic susceptibility. But whether economies, or additional expenses, both are so small in comparison to the total cost of the plant operation and upkeep that in calculating profit we can assume constant cost of production. The line of production cost may, therefore, be drawn parallel to the axis of abscissas (see Fig. 12). It should be borne in mind in this latter connection that the investigation is ordinarily confined to a fairly short range near the maximum value for economic enrichment.

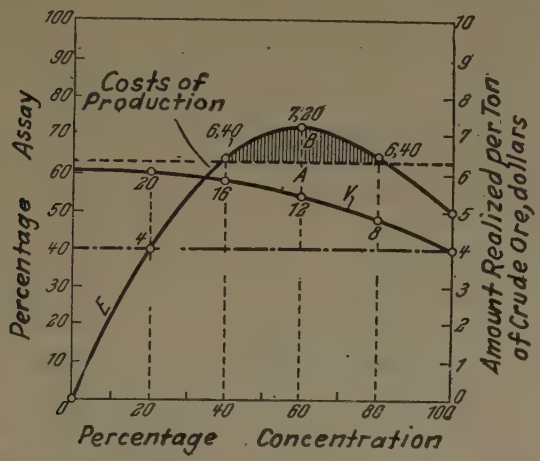


FIG. 12.—RETURN IN DOLLARS PER TON OF CRUDE ORE.

A number of facts may be read from Fig. 12:

1. The maximum of curve $E$ marks the position of greatest possible profit per ton of crude ore under the conditions upon which the chart is plotted. Its ordinate cuts the axis of abscissas at the point of most economic concentration and the intersection of the ordinate with curve $V$ gives the corresponding best assay of concentrate and its selling price per ton.

2. The maximum profit is to be read from the length of the line $AB$.

3. The intersection of the ordinate of the maximum point of curve $E$ with the base curve of the chart (not plotted, but corresponding to curve $I$, Fig. 3) shows the poorest layer that may be included in the concentrate.

4. The limits of profitable operation are indicated by the shaded area.

Profit per 100 tons of crude ore is expressed algebraically by the equation: $100X = CV - 100S$, where $X$ = the profit per ton of crude ore, $V$ = the selling price per ton of concentrate, $C$ = per cent. concentration = tons of concentrate obtained from 100 tons of crude

ore, $S$ = the total cost of production per ton of crude ore, including mining and milling. The profit per ton of crude ore is then

$$X = \frac{CV}{100} - S. \tag{11}$$

In the past the principal difficulty in evaluation of this equation lay in determination of the simultaneously best values of the dependent quantities $C$ and $V$. The method of Fig. 12 solves this difficulty.[5]

In Fig. 12 it has been assumed that the selling price of concentrate could be calculated from *one* factor, in this case the metal assay. If, however, bonuses and penalties enter, no fundamental change in the method of representation is necessary. It is only necessary to plot the modifying factors in such a way as to show their influence upon the value of each particular grade of concentrate. This is illustrated in the method of treating freight charges.

## Influence on Profits of Variation in Conditions of Production and Sale of Concentrate

In the preceding discussion it was assumed as a fundamental part of the argument that the ore, production costs and market value of concentrates remained fixed. Practically, of course, no such constancy exists. The ore varies in metal content and in mineralogical composition and structure, market values fluctuate through a greater or less range according to the metal and the times, and production costs, although changing less rapidly and, ordinarily, through a narrow range, are rarely identical from month to month and year to year. Consequently, if the methods of this paper are to have any more than the most limited application, they must be capable of extension to include and integrate this variability.

### Effect of Variation in Character of Feed

When feed assays vary greatly or when there are distinct and significant changes in the petrographic character of the ore, it must be admitted immediately that no general mathematical formulation or method of graphical representation has been discovered. When, however—either

[5] If use makes the reader more accustomed to think of the extent of concentration in bulk effected by a dressing operation in terms of "ratio of concentration," values of this quantity may be used as abscissas, instead of the values of "concentration," in all of the charts thus far discussed. It is to be noted that the relation expressed in equation (2) graphs as a rectangular hyperbola, and that as a result, when the ratio of concentration lies between 1 and 3, the curves are spread out horizontally through a greater distance if values of $C$ are used as abscissas instead of values of $K$. Throughout the balance of the range plotting to value of $K$ gives the greater spread. Graphically, therefore, the best result will be obtained if values of $C$ are used when the critical range (maximum on curve $E$, Fig. 12) lies between 0 and 30, and values of $K$ when the ratio of concentration exceeds 3.33.

because the changes in character of the ore are small or the dressing process is equally efficient over a wide range of feed values—the concentrate and tailing assays remain relatively constant for a considerable range in feed assay, then a definite relation between maximum profit and feed assay will exist. Under such circumstances values of feed assay ($x$) and profit ($E$) may be read from the relation[6]

$$x_0 = z + \frac{100E(x - z)}{VC_{\text{econ}}} \tag{12}$$

where $x_0$ is the feed assay for which a chart like Fig. 12 has been plotted, and $V,C_{\text{econ}}$ and $z$ are values corresponding to the peak of the profits curve on this chart.[7]

## Influence of Freight on Profit

Thus far the effect of freight has not been taken into consideration. If delivery of concentrate is made f.o.b. mine, costs of carriage need not

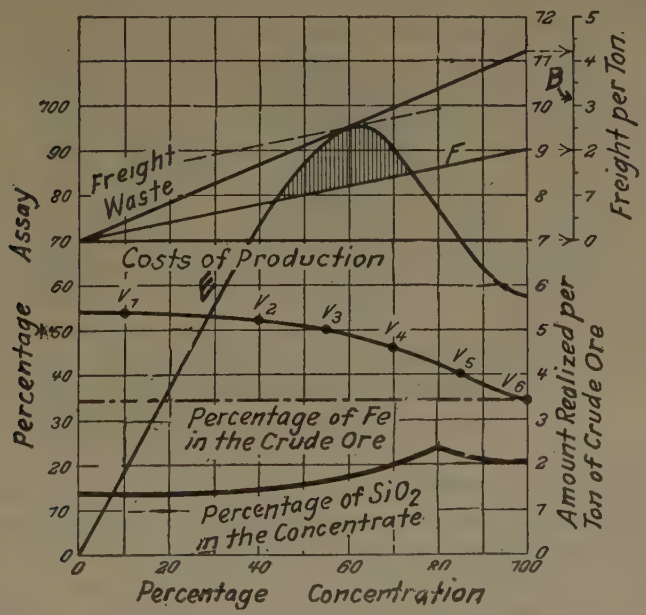


Fig. 13.

be considered, but they must be if delivery is made carriage paid to smelting plant, or c.i.f. harbor smelting plant. This is also true if mine and smelter belong to the same concern. In such cases freight is an additional factor in calculating the production cost. Production of higher

[6] See *Glückauf* (1927) **63**, 194.

[7] The development of this relation is not given by the authors and since, with $E$ made zero, it would seem to indicate that the lowest-grade feed capable of profitable treatment was one whose assay equaled that of the tailing to be produced, it is to be accepted, if at all, with caution.—Editor.

grade concentrate lessens freight costs but diminishes the profit from enrichment. If freight per ton is independent of assay value, then if $B$ (Fig. 13) signifies the freight rate per ton and $C$ the number of tons of concentrate from 100 tons of crude ore, the total freight per 100 tons of crude ore is $BC$. Taking $F$ as the freight per ton of crude, the total freight per 100 tons of crude is $100F$ and $100F = BC$ from which $F = \frac{BC}{100}$. In percentages $F = BC$. Since $B$ is a constant this is a straight-line relation.

Fig. 14 shows the freight-cost line $NM$ plotted above the "cost of production" ($MX = B$ when $C = 100$). Maximum profit is no longer found at the maximum of curve $E$ but where a parallel to $NM$ is tangent to $E$. The coordinates of this point show the economically best enrich-

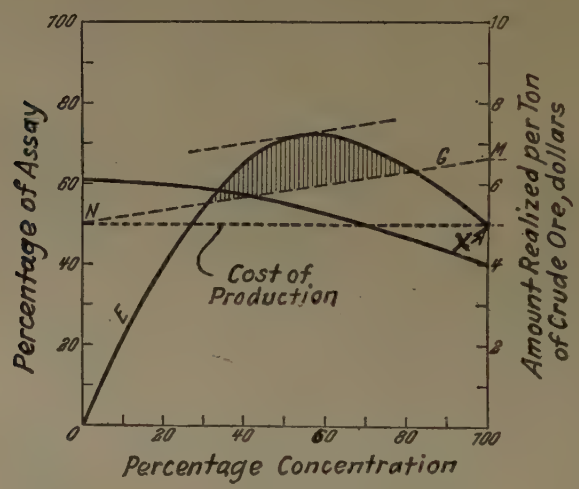


Fig. 14.

ment, and the corresponding freight charge per ton of crude ore (see Fig. 13). With higher freight the point of maximum profit is moved further and further from the maximum of curve $E$, and vice versa. It is well to add a scale for freight, such as line $B$, Fig. 13.

A tangent to curve $E$ through $N$ marks the maximum freight charge before profit disappears and is, therefore, of utility in considering the effect of geographical location on the value of a mine, or the effect on profits of a change in freight rates.

## Influence of Varying Metal Value on Economic Enrichment

The value of concentrate is dependent primarily upon its metal content. Neglecting for the moment the effect on value of impurities, a concentrate is to be considered a salable product whenever the value of the pure metal content is great enough to cover the cost of its extraction

and disposal. Beside actual smelting costs, this includes the expenses incurred in transit from mine to smelter, mine and dealer's profits, customs, duties and freight on the metal. All of these factors are similar in that they are increased in proportion to the bulk of concentrate smelted.[8] If we denote this combined expense per ton of concentrate as $S$, the assay of concentrate as $y$, and the price of the metal per assay unit as $P$, the criterion of salable concentrate may be expressed in the formula $yP = S$. From this may be deduced that the smelter will have an interest in buying ore only when the assay exceeds $y_0 = \frac{S}{P}$. If $V$ is the selling price per ton of concentrate, $V = yP - S$. The return per ton of crude ore is

$$E = CV = CyP - CS.$$

In this equation, $Cy$ = weight of metal in the concentrate from a ton of crude ore, $CyP$ = the value of this metal at current quotations, and $CS$ = the total smelting, refining and marketing cost of $C$ tons of concentrate. When $E$ exceeds production costs, *i. e.*, the sum of the costs of mining and dressing ($L = G + A$), then the mine can be worked at a profit. Therefore, for profitable operation, the following relation must hold:

$$\underbrace{X}_{\text{Profit per ton of crude ore}} = \underbrace{CyP - SC}_{\text{Return from concentrate per ton of crude ore}} - \underbrace{L}_{\text{Mining and dressing expense per ton of crude ore}} \qquad (13)$$

In plotting this relation, monetary values had best be omitted and the weight of metal taken as representative of its value.

Equation (13) then becomes

$$\frac{X}{P} = Cy - \frac{CS}{P} - \frac{L}{P} \qquad (14)$$

or, since

$$\frac{S}{P} = y_0$$

$$\frac{X}{P} = C(y - y_0) - \frac{L}{P} \qquad (15)$$

The enrichment characteristic shows a number of products of different value. Assuming each product to be sold separately the one of lowest value sold would be the one with an assay of $y_0$. Lower grade materia would be marketed at a loss. Hence, in order to obtain maximum return, and, therefore, maximum profit from a concentrating operation, no product should be included in the concentrate whose assay is less

[8] This must be understood as an assumption not ordinarily in accord with the facts. —EDITOR.

than $y_0$. In Fig. 15 this maximum return is shown as the shaded area under the base curve (curve I, Fig. 3) of the enrichment characteristic. This area is equal to $Cy$ and must be larger than the area $Cy_0$, which shows the costs of freight on concentrate, smelting, refining and marketing in equivalent weights of metal. The difference in areas gives the return, which must be greater than the costs for mining and dressing, the equivalent metal weights for which are shown in the rectangle drawn below the axis of abscissas.

Fig. 15 shows the connection between metallurgical enrichment and economic factors. Production costs are again assumed to be constant,

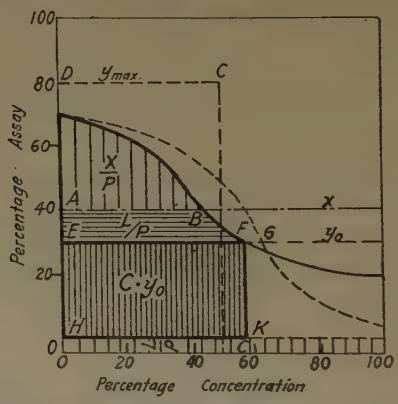


FIG. 15.—RELATION BETWEEN METALLURGICAL ENRICHMENT AND ECONOMIC FACTORS.

and from the net yield area $(Cy - Cy_0)$ must again be deducted the production cost $\left(\frac{L}{P}\right)$ in order to determine the profit $\left(\frac{X}{P}\right)$. It may be seen that with a given base curve, the magnitude of the yield area is determined by the value $y_0$. If $y_0$ is high, the gross-yield area $(Cy)$ is diminished because of a correspondingly decreased value of $C$. If, on the other hand, $y_0$ decreases, the gross-yield area increases with the corresponding increase in the permissible value of $C$. Since $y_0 = \frac{S}{P}$ the situation of line $y_0$ is determined by the costs of smelting, refining and marketing as well as by the market price. The effect of these two factors is in opposite directions. With $S$ constant, a declining market causes $y_0$ to increase, and mill concentrate should be raised in grade with consequent reduction in weight. On a rising market $y_0$ diminishes, *i. e.*, lower grade concentrate can be sold, and the gross-yield area increases correspondingly. Similar reasoning applies to variation in $S$.

Changes in the costs of mining and dressing have no influence on the value $y_0$. Their variations influence profit only, and therefore have no effect in determining the grade of concentrate to be made.

## Concentrate Assay of Zero Value

The principal difficulty in the determination of $y_0$ lies in ascertaining the variations in selling price of concentrate. This involves consideration of commercial smelting schedules, which in the simplest case, are of the form:

$$V = fP(y - y_a) - H \tag{16}$$

where $P$ = the quoted price per unit of metal, $f$ = a percentage factor by which the market price is diminished, $y_a$ = the loss of metal in smelting, expressed as a percentage of the weight of concentrate smelted, and $H$ = the costs of smelting. The lower limit of assay for salable concentrate ($y_0$) is obtained by substituting $y_0$ for $y$ in equation (16), making $V = 0$. This gives

$$y_0 = y_a + \frac{H}{fP} \tag{17}$$

As a rule, however, such simple mathematical statements have very definite limits, and as soon as $V$ ceases to bear a straight-line relation to $y$, the calculation of the assay of concentrate of zero value runs into difficulties, and may become impossible, if the schedule involves a number of variables entering into the final valuation $V$. Another disadvantage in such algebraic calculation lies in the fact that, in determining the assay of concentrate of zero value, it is not at the same time known what concentrate assay and what degree of concentration must be attained in order to assure maximum economic success.

All of these difficulties have been overcome by the economic characteristic shown in Fig. 15. The value $y_0$ for this diagram is read from the intersection of the ordinate of the maximum of the gross-yield curve ($E$, Fig. 12) with the base curve (curve $I$, Fig. 3). The field of the graphical method is, therefore, much wider than that of the purely algebraic calculation.

## Relation between Technical Enrichment Effect and Economic Result

Fig. 15 proves the connection between economic success and the technical enrichment effect as well as showing exactly how far an enrichment process can yield salable products with economic success. In the discussion of absolute efficiency and its derivation from the enrichment characteristic, the line of the feed assay was shown to mark the lower limit of concentrate assay, since only the metal represented by the area above this line and under the base curve constitutes enrichment with respect to the feed. In Fig. 15 the line of the concentrate assay

of zero value ($y_0$) is similarly the economic lower limit for here only the area above and between this line and the base curve represents metal on which a profit is possible. The maximum values of concentration ($C$) from both technical and economic aspects are determined by intersections with the base curve, the first of the line $x$ (= feed assay), the second of the line $y_0$. If the feed assay and $y_0$ are the same, these two values of $C$ coincide. Practically, this is the case if the metal content of the crude ore would just pay the costs of freight on ore, smelting, refining and marketing. If, however, the economic zero line is lower than the average feed assay, material of lower grade than the feed may be put into the concentrate, *i. e.*, the economic optimum permits a larger concentration and a lower concentrate assay than that indicated by the maximum of the technical enrichment diagram. If we trace out the relation between the base curve and the corresponding positions of the absolute efficiency, we find, in such a case, that absolute efficiency has passed its maximum before the maximum economic success has been reached. If, on the other hand, crude ore cannot be sold under the schedule, the economic optimum is attained with a smaller concentration and a higher assay value than the technical optimum.

It may thus be seen that mere comparison of the possible ratios of concentration in a given dressing process with the corresponding absolute efficiencies does not produce any certain information as to economic success.[9] If, however, two or more processes are to be compared, the maximum absolute efficiencies are indicative of the relative economic successes, a fixed production cost being assumed. This is shown in Fig. 15. The dotted base curve, for example, shows a process with higher maximum absolute efficiency than that indicated by the full curve. The result is an increase in the area under the curve and above $y_0$, and this is the area that measures profits.

The close connection between economic and technical enrichment effects which are shown diagrammatically by the partly overlapping areas of the enrichment effect[10] and the gross yield[11] suggests the idea of establishing a characteristic of economic efficiency ($\eta_e$) similar to that already established for technical efficiency (equations 6 and 7). In Fig. 15 economic success may be expressed in weight of metal as $C(y - y_0)$, and profit as $C(y - y_0) - \frac{L}{P}$. The ideal economic effect is shown in Fig. 15. as the rectangle *EFCD*. The algebraic expression for this area is $C_{opt}(y_{max} - y_0)$. (In this ideal case the production cost

[9] Since with a given process, under the assumption of the authors, the base curve is invariable.—Editor.

[10] Area between base curve and line of feed assays.—Editor.

[11] Area between base curve and $y_0$ line, Fig. 15.—Editor.

is considered zero.) Dividing profit by this ideal value gives for the index of economic efficiency:

$$\eta_e = \frac{C(y - y_0) - \frac{L}{P}}{C_{opt}(y_{max} - y_0)} \tag{18}$$

This formula may be used to test any enrichment result, since it embraces every contributory factor, both technical and economic. Changes in flow sheet and their influence on the economic result may be followed easily by plotting corresponding base curves on Fig. 15 and substituting corresponding values in equation (18). Changes in selling price of concentrate involve changes in the position of $y_0$, but this determined, the quantities for equation (18) are again available.

## DISCUSSION

A. C. Halferdahl, Ottawa, Ont. (written discussion).—This paper is interesting but there is one part in which the application of the methods is probably open to question. On page 440, we find, "The method of absolute efficiency is applicable to analysis of performance in sizing. Thus, in the Dorr classifier consider the raw discharge concentrate and the overflow tailing. Let the percentages of oversize in feed, sand and overflow be considered the assay values, $x$, $y$ and $z$ respectively. Then from equations 6, 7, 8, the absolute efficiency may be written:

$$\eta = \frac{\text{recovery of oversize in the coarse material} - \text{concentration of coarse material}}{\text{undersize in the feed}}$$

. . . and the recovery must be calculated by applying the results of the screen analysis, *i.e.*, from the values $x$, $y$ and $z$."

Attention is directed to the use of screen sizing tests for evaluating classifier efficiency, though undoubtedly we should measure classifying efficiency by the most perfect classification possible. An ore particle of high gravity may be classified with a much larger gangue particle without prejudice to real classifying efficiency.

In these days of selective flotation, when fine-grinding mills are operated in circuit with classifiers, which are usually of the Dorr type, it may easily be that adequate liberation of the sulfide portion of an ore from the gangue occurs at some specified size, which is considerably larger than the size necessary to liberate the associated sulfides. In such cases, screen sizing tests often give valuable comparisons on products of different machines on the same ore, but comparisons of screen sizing tests and efficiencies calculated therefrom on different ores must be made with caution when screen sizing tests only are available.

The chief interest is obviously the most profitable degree of liberation of valuable minerals and the securing of such results may rest in a large degree upon the choice of classifier. To clarify these statements, certain data are submitted, which were obtained during the first year of operation (1924) of the Anyox mill of the Granby Consolidated Mining, Smelting & Power Co. The ore was a low-grade copper ore in which the copper occurred as chalcopyrite associated with pyrrhotite and pyrite in an altered gangue. Gold and silver values were very low. It was early realized that the intimacy of association of the sulfide minerals was fundamental and that successful flotation treatment would be largely conditioned upon effective liberation of the chalcopyrite from its associated minerals.

The mill as constructed contained two types of classifiers, one a Dorr classifier and the other of the Esperanza type. The two kinds of classifiers were of practically

TABLE 2

*Screen Analyses*

*Overflow of Esperanza-type Classifier*

| Mesh | Weight | | Assays, Per Cent. | | | | Weight of Copper | | Weight of Iron | | Weight of Sulfur | | Weightof Insoluble | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Per Cent. | Cumulative, Per Cent. | Cu | Fe | S | Insol. | Per Cent. | Cumulative, Per Cent. | Per Cent. | Cumulative, Per Cent. | Per Cent. | Cumulative, Per Cent. | Per Cent. | Cumulative, Per Cent. |
| + 35 | 0.93 | 0.93 | 0.38 | 8.4 | 2.3 | 71.9 | 0.88 | 0.88 | 2.15 | 2.15 | 0.94 | 0.94 | 4.62 | 4.62 |
| + 48 | 2.88 | 3.81 | | | | | | | | | | | | |
| + 65 | 4.60 | 8.41 | 0.62 | 9.3 | 2.8 | 69.1 | 1.73 | 2.61 | 2.87 | 5.02 | 1.38 | 2.32 | 5.36 | 9.98 |
| +100 | 10.32 | 18.73 | 0.97 | 10.3 | 4.4 | 67.4 | 6.07 | 8.68 | 7.14 | 12.16 | 4.85 | 7.17 | 11.73 | 21.71 |
| +150 | 12.84 | 31.57 | 1.62 | 18.6 | 10.7 | 56.8 | 12.62 | 21.30 | 16.04 | 28.20 | 14.67 | 21.84 | 12.30 | 34.01 |
| +200 | 7.46 | 39.03 | 2.02 | 19.1 | 11.5 | 55.5 | 9.14 | 30.44 | 9.57 | 37.77 | 9.16 | 31.00 | 6.98 | 40.99 |
| −200 | 60.97 | 100.00 | 1.88 | 15.2 | 10.6 | 57.4 | 69.56 | 100.00 | 62.23 | 100.00 | 69.00 | 100.00 | 59.01 | 100.00 |

Original Assays: Cu, 1.65 per cent.; Fe, 14.9; S, 9.4; Insol., 59.3.

*Overflow of Dorr Classifier*

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| + 35 | 0.78 | 0.78 | 0.33 | 7.7 | 1.8 | 71.2 | 0.66 | 0.66 | 1.64 | 1.64 | 0.77 | 0.77 | 4.40 | 4.40 |
| + 48 | 2.61 | 3.39 | | | | | | | | | | | | |
| + 65 | 4.79 | 8.18 | 0.56 | 8.9 | 2.5 | 68.4 | 1.57 | 2.23 | 2.67 | 4.31 | 1.51 | 2.28 | 5.97 | 10.37 |
| +100 | 10.60 | 18.78 | 1.11 | 13.1 | 6.6 | 63.1 | 6.89 | 9.12 | 8.71 | 13.02 | 8.83 | 11.11 | 12.19 | 22.56 |
| +150 | 11.56 | 30.34 | 1.61 | 16.4 | 9.5 | 59.2 | 10.90 | 20.02 | 11.89 | 24.91 | 12.39 | 23.50 | 12.47 | 35.03 |
| +200 | 7.39 | 37.73 | 2.04 | 21.2 | 12.1 | 50.8 | 8.83 | 28.85 | 9.83 | 34.74 | 11.28 | 34.78 | 6.84 | 41.87 |
| −200 | 62.27 | 100.00 | 1.95 | 16.7 | 8.3 | 51.2 | 71.15 | 100.00 | 65.26 | 100.00 | 65.22 | 100.00 | 58.13 | 100.00 |

Original Assays: Cu, 1.71 per cent.; Fe, 15.9; S, 7.9; Insol., 54.9.

| Mesh | Esperanza-type Classifier | | | | Dorr Classifier | | | |
|---|---|---|---|---|---|---|---|---|
| | Sands | | Feed | | Sands | | Feed | |
| | Per Cent. Weight | Cumulative Per Cent. Weight | Per Cent. Weight | Cumulative Per Cent. Weight | Per Cent. Weight | Cumulative Per Cent. Weight | Per Cent. Weight | Cumulative Per Cent. Weight |
| + 35 | 11.23 | 11.23 | 6.90 | 6.90 | 12.38 | 12.38 | 10.68 | 10.68 |
| + 48 | 13.23 | 24.46 | 7.51 | 14.41 | 12.76 | 25.14 | 9.83 | 20.51 |
| + 65 | 14.84 | 39.30 | 10.03 | 24.44 | 16.68 | 41.82 | 12.45 | 32.96 |
| +100 | 23.76 | 63.06 | 17.48 | 41.92 | 25.35 | 67.17 | 19.80 | 52.76 |
| +150 | 19.74 | 82.80 | 12.07 | 53.99 | 14.27 | 81.44 | 11.94 | 64.90 |
| +200 | 5.05 | 87.85 | 7.47 | 61.46 | 5.72 | 87.16 | 6.73 | 71.43 |
| −200 | 12.15 | 100.00 | 38.54 | 100.00 | 12.84 | 100.00 | 28.57 | 100.00 |

Fifty per cent. of the classifier sands was lifted by the electromagnet, in each case. Meshes are Tyler standard.

TABLE 3

*Overflow of Esperanza-type Classifier*

| Mesh | Per Cent. Weight on This Mesh | | Cumulative Weight, Per Cent. Total | | Per Cent. Weight This Mesh of Float in Non-magnetic | Per Cent. Weight This Mesh of Sink in Non-magnetic | Cumulative Weight Per Cent. Total Float in Non-magnetic | Cumulative Weight Per Cent. Total Sink in Non-magnetic | Assays on Magnetic Material | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Magnetic Material | Non-magnetic Material | Magnetic Material | Non-magnetic Material | | | | | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. |
| + 35 | 32.1 | 67.9 | 0.30 | 0.63 | 98.54 | 1.46 | 2.81 | 0.04 | 0.58 | 12.4 | 3.4 | 63.4 |
| + 48 | 22.8 | 77.2 | 0.96 | 2.85 | | | | | | | | |
| + 65 | 19.9 | 80.1 | 1.88 | 6.53 | 97.33 | 2.67 | 6.39 | 0.14 | 0.92 | 18.2 | 6.5 | 57.0 |
| +100 | 17.5 | 82.5 | 3.69 | 15.04 | 93.11 | 6.89 | 14.31 | 0.73 | 1.15 | 21.8 | 8.2 | 48.8 |
| +150 | 30.4 | 69.6 | 7.59 | 23.98 | 83.23 | 16.77 | 21.75 | 2.23 | 1.31 | 36.1 | 17.0 | 36.5 |
| +200 | 24.7 | 75.3 | 9.43 | 29.60 | 79.78 | 20.22 | 26.23 | 3.37 | 1.24 | 41.6 | 17.4 | 28.4 |
| −200 | 13.2 | 86.8 | 17.48 | 82.52 | | | | | 0.59 | 43.4 | 19.6 | 28.8 |

| Mesh | Assays on Non-magnetic Float Material | | | | Assays on Non-magnetic Sink Material | | | | Per Cent. Cu This Mesh in Magnetic Material | Per Cent. Cu This Mesh in Float Material | Per Cent. Cu This Mesh in Sink Material | Cummulative Per Cent. Cu in Magnetic Material | Cumulative Per Cent. Cu in Float Material | Cumulative Per Cent. Cu in Sink Material |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. | | | | | | |
| + 48 | 0.21 | 5.7 | 0.9 | 75.4 | 8.26 | 26.3 | 26.7 | 31.1 | 45.4 | 34.4 | 20.2 | 0.40 | 0.30 | 0.28 |
| + 65 | 0.25 | 6.4 | 1.1 | 73.6 | 11.20 | 31.2 | 31.0 | 19.0 | 29.7 | 31.5 | 38.8 | 0.91 | 0.84 | 0.96 |
| +100 | 0.21 | 5.8 | 1.0 | 75.7 | 10.68 | 36.7 | 38.8 | 11.2 | 20.8 | 16.6 | 62.6 | 2.17 | 1.85 | 4.76 |
| +150 | 0.25 | 4.9 | 0.8 | 78.0 | 9.28 | 40.8 | 43.6 | 4.8 | 24.4 | 8.9 | 66.7 | 5.24 | 2.97 | 13.19 |
| +200 | 0.20 | 4.6 | 1.1 | 79.0 | 10.44 | 39.5 | 42.4 | 6.6 | 15.2 | 5.9 | 78.9 | 6.63 | 3.51 | 20.40 |
| −200 | | | | | | | | | 4.1 | 95.9 | | 9.48 | 90.52 | |

*Overflow of Dorr Classifier*

| Mesh | Per Cent. Weight on This Mesh | | Cumulative Weight Per Cent. Total | | Per Cent. Weight This Mesh of Float in Non-magnetic | Per Cent. Weight This Mesh of Sink in Non-magnetic | Cumulative Weight Per Cent. Total Float in Non-magnetic | Cumulative Weight Per Cent. Total Sink in Non-magnetic | Assays on Magnetic Material | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Magnetic Material | Non-magnetic Material | Magnetic Material | Non-magnetic Material | | | | | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. |
| + 35 | 31.7 | 68.3 | 0.25 | 0.53 | 99.11 | 0.89 | 2.51 | 0.02 | 0.48 | 11.6 | 2.9 | 65.9 |
| + 48 | 23.3 | 76.7 | 0.86 | 2.53 | | | | | | | | |
| + 65 | 18.7 | 81.3 | 1.76 | 6.42 | 97.28 | 2.72 | 6.29 | 0.13 | 0.91 | 17.1 | 5.5 | 58.2 |
| +100 | 16.9 | 83.1 | 3.55 | 15.23 | 88.64 | 11.36 | 14.10 | 1.13 | 1.20 | 31.0 | 13.2 | 40.6 |
| +150 | 21.9 | 78.1 | 6.08 | 24.26 | 83.93 | 16.07 | 21.68 | 2.58 | 1.27 | 37.5 | 16.8 | 33.8 |
| +200 | 24.9 | 75.1 | 7.92 | 29.81 | 77.92 | 22.08 | 26.00 | 3.81 | 1.21 | 47.6 | 18.7 | 20.5 |
| −200 | 14.1 | 85.9 | 16.70 | 83.30 | | | | | 0.53 | 44.1 | 20.8 | 28.0 |

| Mesh | Assays on Non-magnetic Float Material | | | | Assays on Non-magnetic Sink Material | | | | Per Cent. Cu This Mesh in Magnetic Material | Per Cent. Cu This Mesh in Float Material | Per Cent. Cu This Mesh in Sink Material | Cumulative Per Cent. Cu in Magnetic Material | Cumulative Per Cent. Cu in Float Material | Cumulative Per Cent. Cu in Sink Material |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. | Per Cent. Cu | Per Cent. Fe | Per Cent. S | Per Cent. Insol. | | | | | | |
| + 48 | 0.21 | 6.2 | 1.1 | 73.4 | 8.52 | 31.1 | 30.3 | 30.0 | 36.7 | 46.4 | 16.9 | 0.24 | 0.31 | 0.11 |
| + 65 | 0.22 | 6.3 | 0.8 | 73.0 | 9.67 | 32.7 | 36.4 | 15.6 | 30.4 | 31.3 | 38.3 | 0.72 | 0.80 | 0.71 |
| +100 | 0.18 | 5.9 | 0.6 | 75.0 | 8.16 | 37.8 | 41.0 | 10.8 | 18.3 | 12.0 | 69.7 | 1.98 | 1.63 | 5.51 |
| +150 | 0.18 | 5.0 | 0.7 | 77.7 | 9.68 | 39.0 | 43.1 | 6.5 | 17.2 | 7.3 | 75.5 | 3.85 | 2.43 | 13.74 |
| +200 | 0.17 | 4.9 | 0.7 | 77.5 | 9.92 | 39.4 | 42.5 | 6.0 | 14.7 | 4.9 | 80.4 | 5.15 | 2.86 | 20.84 |
| −200 | | | | | | | | | 3.8 | 96.2 | | 7.85 | 92.15 | |

the same settling area and were operated in closed circuit with mills handling the same tonnage of ore each.

The classifier products and feed in each case were sampled for several days and the samples investigated were reliable averages. The first procedure was to screen-size each product. The results are given in Table 2. Subsequent detailed results are given for the overflow products only out of respect to the reader, although the classifier feeds and sands were investigated.

From appearances, it might be concluded that the Dorr classifier gave a slightly better liberation of mineral in the overflow. This could be due to the small difference in the ore treated. However, the following tests were made on each screen size of the classifier overflow. First a magnetic portion was separated carefully by means of a small electromagnet from each screen size, including the −200-mesh fines. The amount lifted by the magnet depends upon the strength of the field, and slightly different results would be obtained with a different magnet. Then by use of methylene iodide (sp. gr., 3.2), the nonmagnetic portion of each mesh was separated into sink and float portions, but this separation was omitted on the −200-mesh fines. Every portion separated was weighed and assayed and the results are given in Table 3.

A few facts stand out sharply. Gangue and sulfides are fairly intimate, but the sulfides are more intimate in their association. It is necessary to secure extremely efficient classification in order to eliminate excessive grinding of gangue, yet liberation of the maximum amount of sulfides attached to the gangue must be obtained in order to make a satisfactory concentrate and tailing. The gangue is pulverized selectively in both cases, but more so with the Esperanza machine. The copper-pyrrhotite association is broken up only at sizes finer than 200 mesh. Fortunately the mechanical floculating effect of magnetic particles occurs, consequently such particles are kept in the grinding circuit longer. Losses in tailings may be expected to show in the coarser sizes because of the intimate chalcopyrite attachment and because pyrrhotite is quite easily depressed in the flotation and carries the copper with it. One interesting feature is that the gangue not lifted by the magnet is reasonably free of copper at 65 mesh. This again points to larger classifier capacity and makes it necessary to secure higher efficiency in order to eliminate gangue as rapidly as possible from the circuit once it is free of copper.

Microscopic examination of each of the products separated was made. It appeared that the chalcopyrite-pyrite association was broken at about 150 mesh. This was practically confirmed by other work. It also follows that if the concentrate does not run higher than 10 per cent copper, no pyrite is being sent into the tailings.

The data appear to show that the Dorr classifier gave a little better liberation of minerals than the Esperanza type, but the chief conclusion arrived at was that the classifier capacity was entirely inadequate. A larger classifier would permit a denser overflow and thereby increase the hindered-settling effect, which is desirable on this ore. Larger classifiers were installed subsequently, with beneficial results.

With these facts before us, just how may we arrive at some figure or figures that will really represent the efficiency of the arrangement? Reference to screen sizing and efficiencies calculated therefrom gives information but it is not conclusive. The writer assumed for mill purposes that −150-mesh nonmagnetic copper was all liberated and that the percentage of such copper of the total copper in the overflow represented the "efficiency" of the grinding-classifier system. This is not right, however, when we consider that much gangue may be and here actually was needlessly and wastefully ground finer than necessary to secure adequate liberation of the chalcopyrite.

Further discussion of the problem of classifier efficiency and of efficiencies of classifier-grinding arrangements should be helpful.

E. Bierbrauer (written discussion).—The capacity measurement of a classifier as proposed by us is based on the idea that the classifier must separate the material coming from a grinding process in such a manner that only oversize is returned to the reduction process. But if we consider, as A. C. Halferdahl has done in his interesting letter, the disintegration power with its fine differentials as the essential object of the investigation, then naturally the degree of separation proposed by us is suitable only to a limited extent. In view of the importance of these questions in practical operation, the statements of A. C. Halferdahl are extraordinarily acceptable, and we would like to express a wish that these problems be carried further by additional investigations.

# Microscopic Studies of Mill Products as an Aid to Operation at the Utah Copper Mills

By H. S. Martin,* Garfield, Utah

(San Francisco Meeting, October, 1929)

Although it was known some years ago at the Utah Copper Co. mills that fine grinding improved flotation recoveries, no accurate data were available until recently as to just how far the grinding could be carried economically. In 1923 the ultimate degree of fineness for flotation feed was supposed to be about 10 per cent. on 65 mesh, with approximately 55 per cent. through 200 mesh, which meant that most of the mineral would pass 100 mesh. At this time Garfield and Wilfley tables were used ahead of flotation and a good deal of the coarse mineral removed prior to the ball mill regrind. Shortly afterwards, mill-scale tests developed the fact that on a feed containing not over 10 per cent. +65-mesh material flotation alone would give a copper recovery equal to that obtained by the combination of tables and flotation, but that on much coarser feed the recovery with flotation alone was lowered. This was at a time when all the sulfide minerals were floated if possible, so that the only requisite was to grind fine enough to free the mineral from gangue.

## Earliest Use of Microscopic Examination of Tailings

As early as 1921, the writer had attempted to determine by chemical analysis the relative proportions of copper minerals in tailings from an ore that made extremely poor flotation results. Chemical analysis was not satisfactory or conclusive, and samples of these tailings were sent to the U. S. Bureau of Mines Station at the University of Utah for microscopic examination. The question at that time was to determine, if possible, which copper minerals had been lost and why, but R. E. Head, in his report, revealed other interesting data. He said in part:

> Briefly stated, the mineral particles or grains may be classified into separate groups as follows: 1. Free grains of pyrite, chalcopyrite, chalcocite and bornite, respectively, which contain no other included sulfides; 2. Grains in which all three of the copper sulfides are represented (the core may be of chalcopyrite, partially altered to bornite, these two minerals being entirely surrounded by a shell of chalcocite); 3. Grains composed of equal amounts of bornite and chalcocite or chalcopyrite and chalcocite.
>
> The grains of free mineral particles are perhaps the most numerous, taking the ore as a whole, but it is noticeable that of the grains of combined or associated sulfides

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those in which the core is composed of chalcopyrite with or without bornite, and entirely surrounded by chalcocite are the most numerous in the material up to and including the 100-mesh size. As the core is crushed finer there are, of course, more of these intimately associated mineral grains broken down into individual particles. These types of occurrence of the copper sulfides should be borne in mind when the relative floatability of the respective copper sulfides is considered, since those grains that have a core of chalcopyrite surrounded by chalcocite might logically be expected to behave the same as those composed entirely of chalcocite under like conditions of flotation, and likewise a grain with a core of chalcocite and having a shell of chalcopyrite. The possibilities of the action of grains containing the other mineral associations described also present themselves for discussion and consideration from a standpoint of relative floatability but will not be discussed in this report.

This microscopic examination revealed that more than 60 per cent. of the copper lost was in the form of chalcocite, but no certain reason for the loss was developed at that time.

## Pyrite as Cause of Copper Loss

As the operations at the Utah Copper mine began to cover more area, and lowering of milling costs made profitable the handling of lower grade ores, the grade of concentrate produced became lower and lower until, in 1926, the average for the year was only 17.07 per cent. copper. The principal reason for this lower grade of concentrate was the presence of pyrite in the concentrate, but another reason was that the ore then being mined was predominantly a chalcopyrite ore, whereas early mining operations had opened the lower levels only, where chalcocite predominates. The concentrators were faced with the problem of handling a low-copper heading containing principally chalcopyrite and pyrite for a good many years ahead, or until the upper portions of the mine were removed. In 1924 research work was begun in the laboratory to determine whether pyrite might be rejected without too great a loss of copper. The method first used was to separate the different minerals in Wilfley table concentrate with a pair of tweezers under a low-power microscope. Specimens of apparently pure pyrite so obtained were analyzed for copper and many samples assayed from 0.75 to 1.00 per cent. copper. The conclusions drawn from this work were that copper existed in the pyrite in solid solution and not as inclusions, and that rejection of pyrite would necessarily entail a loss of copper, no matter how fine the grinding. Even with such copper loss, the doubling of the copper content in the concentrate would be a paying proposition, therefore the work was continued. Samples of Wilfley table concentrate were sent again to the Bureau of Mines for microscopic examination to check or disprove this theory. R. E. Head's report of this work, under date of June 10, 1925, is in part as follows

In order to obtain accurate data on the copper content of the pyrite, two samples were hand-picked by the aid of the binocular microscope, and only particles that

appeared to be pure pyrite were selected. One of these samples was submitted to the Department analyst, Mr. Christensen, for determination of copper by chemical methods, and the other was made up in briquet form for mechanical microscopic analysis in which the method described in Bureau of Mines *Reports of Investigation* No. 2257 was employed. This method is known as the Rosinal method and has proved satisfactory for mechanical analysis of mixed sulfide minerals.

The results of the chemical and microscopic analyses checked quite closely, the former showing a copper content of 0.25 per cent. and the microscopic count 0.28 per cent.

The pyrite particles used in this portion of the work were of +20-mesh size and the fact that the material was representative is evidenced by the closeness of the results obtained.

This work indicates quite conclusively that the copper content of the Utah Copper pyrite is comparatively small.

### *Forms in Which Copper Is Associated with the Pyrite*

Copper is associated with the Bingham pyrite in two distinct forms: (a) as included particles of copper-bearing minerals, and (b) as films of chalcocite on the outer surface of the pyrite grains similar to that observed on the pyrite from some porphyry deposits in the Southwest.

The included copper minerals are of most importance in view of the objective contemplated, since it is obvious that they must be liberated during crushing. Failure to do so would involve an additional loss of copper in the tailing, if pyrite were "dropped" during flotation.

By far the greater portion of the included sulfide particles in the pyrite consists of chalcopyrite, but occasional particles of chalcocite and bornite were found in the material examined. There appears to be no regularity in the distribution of the copper minerals in the pyrite, some grains containing but one inclusion but occasional grains of pyrite were found with two or more included particles of copper-bearing minerals.

### *Possibility of Liberating Included Copper Minerals by Crushing*

From microscopic measurements of the copper-bearing mineral particles included in the pyrite grains it is estimated that fully 50 per cent. of them would be liberated by grinding to the extent now practiced at the Magna and Arthur plants of the Utah Copper Co. The included copper minerals do not have the appearance of being true intergrowths with the pyrite but give the impression of having been mechanically included in the pyrite at the time of its formation. Their presence, therefore, constitutes zones of weakness in the pyrite which would fracture more readily than would be the case with homogeneous pyrite. That practically all the included particles are liberated under present grinding practice is indicated by microscopic examination of briquets made up of the flotation feed. Such inclusions as remain locked are of extremely small size (smaller than 300 mesh) and from a standpoint of copper content would be of negligible importance.

This work proved conclusively that entirely barren pyrite could be eliminated if the grinding were fine enough, and completely negatived the idea of solid solution. The problem then became one of finding a method to reject the pyrite in flotation. Some work had been done with

cyanide in alkaline circuit, but results were not promising with the old flotation reagents. A new reagent called "Aerofloat," which was developed in the Utah Copper research laboratory, had been tested for a year or more in acid, alkaline and neutral circuits in the laboratory. This reagent in alkaline circuit showed a consistent tendency to leave iron sulfide in the tailings, even when no specific iron depressor was used. This phenomenon was first noted because of the routine laboratory practice of panning the test tailings for sulfide mineral. The presence of a considerable amount of sulfide minerals in every tailing sample from alkaline tests using Aerofloat at first led to the belief that this reagent was making poor copper recoveries, but actual assays showed just as low tailings as in the tests where all the sulfides had been floated. This laboratory discovery was followed by extensive testing on 400-ton experimental flotation machines, with the result that the Aerofloat consistently made good copper recoveries and concentrate of 6 to 8 per cent. higher grade than was formerly obtained.

At this time, E. L. Tucker of the American Cyanamid Co. was doing research work at the U. S. Bureau of Mines at Salt Lake on the use of cyanide in depressing iron and his reports led to the testing of cyanide again in conjunction with Aerofloat. Good results were obtained with this combination with a few exceptions. During February, 1926, one day's results showed high copper losses in the tailing on the machine where iron was being rejected, and the theory was advanced that with this particular type of ore, iron and copper minerals were closely associated and the iron had carried copper into the tailing. This was a possibility, since the grinding at that time was over 20 per cent. material on 100 mesh. Samples of this tailing were sent the Bureau of Mines and Mr. Head again reported on March 20, 1926, his microscopic examination as follows:

The entire surface was first examined in order to obtain an idea of the extent to which grains of pyrite containing included copper minerals occurred. This cursory examination indicated that associated pyrite-copper mineral associations were exceedingly rare and a detailed count was therefore made of three squares of the briquet.

The result of this work was as follows:

| | |
|---|---|
| Total grains counted | 1013 |
| Number of included grains | 5 |

The amount of copper represented in these five included grains is obviously negligible and substantiates former work on Utah Copper ore, thus further emphasizing the statement that elimination of pyrite would result in no additional copper loss due to the presence of included copper minerals in the pyrite.

Attention was next given to an examination of the sulfides concentrated from the tailing. This granular product was spread over the surface of cross-section paper in a layer one particle thick. As the mineral particles of a square were examined, that particular square was checked off by marking with a pencil to avoid duplication in counting.

In looking over the entire product, probably in excess of 10,000 particles, it was noted that a surprisingly large number of the chalcocite grains had some portion of their surface covered with what appeared to be gangue material of a soft nature. The extent to which the minerals were contaminated varied from a mere trace, in some cases, up to 75 per cent. of the entire surface of the particular particle observed.

In order to gain some quantitative idea of the number of copper-bearing grains so contaminated, numerous squares, selected at random, were counted and those particles in which more than 25 per cent. of the surface was obscured were listed as coated grains.

In all 500 grains of copper mineral were counted, of which 345, or 69 per cent., were contaminated as noted.

There is ample reason to assume that such grains would not float as well as those whose entire surface was exposed, and it is thought that this condition is largely accountable for the losses as shown in the data given on the tests. Under strongly active flotative conditions obtained by reagent regulation, better recoveries of such contaminated grains might be made, resulting, however, in an additional "raising" of pyrite. It may be that under conditions suitable for maximum elimination of pyrite such grains are more easily carried into the tailing.

A sample of the concentrate obtained by panning the tailing was mounted in Canada balsam and examined under the petrographic microscope to identify the mineral which was attached to the surfaces of many of the mineral grains. It turned out to be sericite mica in most cases and in others a clayey substance. This contamination of surfaces by clay and sericite was not confined entirely to the copper minerals but was also noticeable on pyrite surfaces, although to a smaller extent.

No hand specimens of this ore were available for petrographic study, but one would expect that it came from a portion of the deposit in which sericitization was well advanced. That the sericite sticks to the mineral surfaces so tenaciously might be due to the fact that the alteration of feldspar to sericite or clay is accompanied by an increase in volume, thus establishing an intimate bond with the sulfide surfaces through increased pressure. Since the pyrite is crystalline and has hard, smooth and regular surfaces, the sericite would not be expected to adhere so strongly. On the other hand, the copper sulfides, especially the chalcocite, occur in smaller particles having comparatively rough, irregular surfaces, which constitutes an ideal condition for the adherence of such finely divided material as clay or sericite mica.

The conditions described should not be construed as suggesting finer grinding as a means of correcting or overcoming the difficulty. The association of the sulfides with the clay and sericite is purely a matter of surface contamination, and finer grinding, although it might be beneficial, is not advocated as a solution of the problem. It may be that seasonal conditions might be a factor worthy of consideration in checking up the behavior of this type of ore. In other words, such an association might be better broken up during crushing if the ore were dry or the reverse might be the most conducive to good liberation. Observation over a period of time might develop something of interest along this line or the possibilities of these two conditions could be tested out on a small scale by producing them in the laboratory.

*Summary*

The work described in this report gives conclusive evidence regarding two facts, viz.: (1) that the extent to which inclusions of copper minerals exist in Utah Copper pyrite is negligible when the feed is ground to the size used in the tests under consideration; (2) that sericite mica and clay adhere to the surfaces of the sulfides, thus probably lowering their normal rate of floatability, which would account for the increased copper loss when differential separation of iron and copper is attempted on this particular type of ore.

## Fine Grinding to Increase Copper Recovery

This proved, of course, that the excessive copper loss was not caused by inclusions in the pyrite, and suggested the need for finer grinding, as Mr. Head suggested, violent mechanical agitation during flotation, or chemical treatment, to remove the films of sericite. Since finer grinding would certainly yield better copper recovery and cleaner pyrite rejection, this seemed to be the most economical solution of the problem. With increased grinding and classifying capacity which was later installed, such extremely high tailing losses on clean sulfide ores have never recurred. From data available in 1926 and 1927, the ultimate economical point for grinding flotation feed was thought to be about 10 per cent. +100-mesh material, which would mean 65 per cent. of material through 200 mesh. This was as fine a feed as had ever been produced by the mills over any period of time and no plant results were obtainable on much finer grinding, but it was assumed that to go finer would be too expensive an operation.

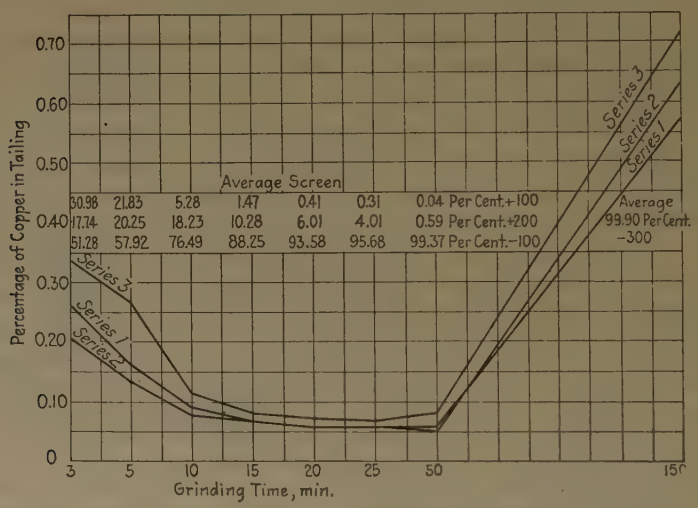
Both mills of the Utah Copper Co. gave high recoveries and a good grade of concentrate during the year 1927 and up to the middle of September, 1928. At this time tonnage was increased to such a point that the flotation feed ranged from 26 to 30 per cent. of +100-mesh material, with a consequent sharp decrease in copper recovery. The management then decided to enlarge the grinding capacity of both plants and by January, 1929, work was under way for the addition of more ball mills and classifiers.

The metallurgical department previously had considered the possibility of equipping a laboratory for microscopic work at the plant, but the expense and time it would take to train someone for the work made it appear more feasible to use the equipment and trained men already available at the Bureau of Mines in Salt Lake. If all the companies should use the microscopic laboratory of the Bureau, the amount of work to be done would necessitate enlargements of both equipment and personnel. Through the efforts of Dorsey A. Lyon, a cooperative microscopic laboratory, supervised by Mr. Head, was finally agreed upon, several mining and smelting companies entering into an agreement to help finance such a laboratory. We were particularly anxious to have a complete microscopic examination made of mill tailings and concentrate while the feed was relatively coarse, so that the results could be compared with similar data taken after the new equipment was put into operation. Such data would give definite information as to just what efficiency was being attained both on the recovery of the different copper minerals and on the rejection of pyrite, data on which was up to this time mostly a guess. It had been assumed, from examination of various specimens of ore under low-power microscopes in the Arthur laboratory, that the average com-

position of sulfide copper-bearing minerals was 80 per cent. chalcopyrite, 15 per cent. chalcocite and 5 per cent. covellite and bornite, but more accurate data were desirable.

An extensive series of laboratory tests made in March, 1929, indicated that even finer grinding than 10 per cent. +100 mesh would be profitable and microscopic data would confirm this conclusion. Table 1 shows the results of these laboratory tests plotted as to copper in the tailing with

TABLE 1.—*Results of Laboratory Tests Showing Effect of Grinding on Flotation Recovery, Utah Copper Co.*




varying time of grind. Three samples of ore of widely different character were chosen and ground to sizes ranging from 51.28 per cent. −200 mesh to 99.9 per cent. −300 mesh. The curves show that these ores made tailings ranging from 0.210 per cent. copper to 0.340 per cent. copper when ground to about 31 per cent. +100 mesh. With finer grinding the tailing lines converge until, with 1.47 per cent. +100 mesh, all three ores gave tailings lower than 0.080 per cent. copper. The assay of tailings also decreases rapidly down to the point of 15 min. grinding, but flatten out from there to the 50-min. period. Another interesting result was that with 2½ hr. grinding, tailings from all three ores increased to 0.600 per cent. copper or over. In the light of subsequent microscopic investigations, this extremely high copper loss after long grinding is rather a reversal. Every effort was made to get good results after this time of grinding; reagents were increased, time of float increased and sulfidizing agents added, but tailings were consistently over 50 per cent. copper. It is probable that the poor results were not due to the size of the mineral, but to surface oxidation, which may be checked up later by the use of the microscope.

## Composite Samples Examined by Cooperative Laboratory

As soon as the cooperative laboratory was ready for operation, 30-day composite samples of tailings and concentrate were made from plant operations and screened into +100, +150, +200 and −200-mesh sizes. These samples were submitted to the new laboratory for examination. A report was submitted by R. E. Head and A. L. Crawford after an enormous amount of painstaking work.

The −200-mesh material was divided by elutriation into four different sizes; *i. e.*, −75 and +25 microns, −25 and +10 microns, −15 and +5 microns, −7 and +3 microns. Each of these four divisions was then examined separately under the microscope and counts made of the various sulfide minerals after panning and briquetting. Their report and explanation of the data follows:

The attached data sheets show graphically and also in tabular form the results of microscopic examination of composite samples of concentrates and tailings from the Utah Copper Company mills for a 30-day period.

Table 2.[a]—*Microscopic Determination of Distribution of Sulfide Minerals in Concentrates and Tailings from the Utah Copper Co. Composite Samples for a 30-day Period*[b]

| Minerals | +100 Per Cent. | +150 Per Cent. | +200 Per Cent. | −75 + 25 Per Cent. | −25 + 10 Per Cent. | −15+5 Per Cent. | −7 + 3 Per Cent. |
|---|---|---|---|---|---|---|---|
| Arthur Mill Concentrates | | | | | | | |
| Pyrite | 29.85 | 29.26 | 23.22 | 12.35 | 4.40 | 1.40 | 0.75 |
| Chalcopyrite | 55.60 | 53.77 | 59.97 | 66.31 | 71.17 | 82.73 | 87.54 |
| Bornite | 2.68 | 4.36 | 6.97 | 5.64 | 4.18 | 2.40 | 0.98 |
| Chalcocite | 7.65 | 8.95 | 5.91 | 8.62 | 9.24 | 6.59 | 4.07 |
| Covellite | 4.22 | 3.65 | 3.93 | 7.07 | 11.24 | 6.86 | 6.66 |
| Total | 100.00 | 99.99 | 100.00 | 99.99 | 100.23 | 99.98 | 100.00 |
| Arthur Mill Tailings | | | | | | | |
| Pyrite | 88.00 | 89.1 | 90.3 | 96.5 | 97.3 | 97.45 | 96.5 |
| Chalcopyrite | 7.47 | 8.13 | 6.42 | 2.45 | 1.9 | 1.65 | 2.07 |
| Bornite | 1.91 | 0.48 | 0.65 | 0.11 | 0.1 | 0.1 | 0.1 |
| Chalcocite | 2.5 | 2.02 | 2.48 | 0.51 | 0.45 | 0.34 | 0.68 |
| Covellite | 0.55 | 0.24 | 0.22 | 0.37 | 0.37 | 0.42 | 0.6 |
| Total | 100.43 | 99.97 | 100.00 | 99.93 | 100.12 | 99.96 | 99.95 |

[a] Table 6 in Report of 7/29/29.

[b] The sizes below 200 mesh are reported in terms of microns.

The tables and graphs have been developed with the intention of establishing the relationship of the copper and iron in the various products and sizes as they are distributed mineralogically. This plan was adopted in view of the incontrovertible fact that in milling operations copper is lost or recovered in the form of minerals. This statement also holds true in regard to the dropping or elimination of iron, hence the importance of data concerning their mineralogical distribution.

The figures given represent the final results obtained by counting, identifying, measuring, and converting into terms of metals, approximately 200,000 individual mineral particles and covering a size range from 100 mesh (0.147 mm.) to 0.003 mm.

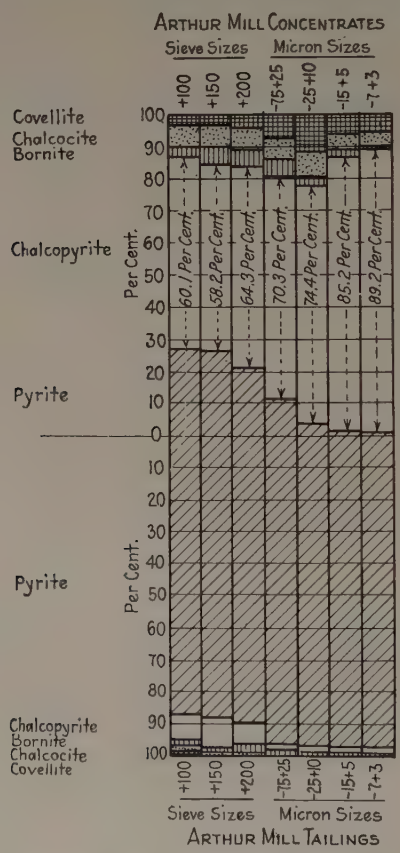



Fig. 1.—Percentage distribution of sulfide minerals in concentrates and tailings.
Plotted from data given in Table 2.

(3 microns), a size much smaller than the openings of a standard 400-mesh sieve (0. 035 mm.).

The graphs [shown here as Figs. 1, 2 and 3] enable a comparison to be made at a glance of the mineralogical composition of the concentrates and tailings. Fig. 1 shows graphically the results in Table 6 [shown here as Table 2], Fig. 2 the results of Table 7 [shown as Table 3] and Fig. 3 the results in Table 8 [shown as Table 4]. They correspond to the figures given in the tables except that in the graphs the figures

for the various minerals are given in terms of volumes whereas the corresponding tables are computed in weights.

The value of the data given in the graphs and tables lies in their interpretation and application to plant operation. It is obvious that the percentage weight distribution of the sulfide minerals in the various products, exclusive of nonsulfide material, is highly essential to an understanding of the grinding size requirements as indicated by the recovery of the several minerals. Table 5 has therefore been prepared and constitutes a summary tabulation of sulfides, sulfide iron, and sulfide copper, showing the weight percentage distribution of each product by recasting the total per cent. of each constituent in the concentrate or tailing to 100 per cent.

The data presented in this report afford ample ground for careful study by the operating departments of the Arthur and Magna mills. Many interesting and valuable conclusions may be drawn as a result of such study and the facts underlying them

TABLE 3.[a]—*Microscopic Determination of Distribution of Copper as Mineralogically Represented in Concentrates and Tailings from the Utah Copper Co. Composite Samples for a 30-day Period*[b]

| Minerals | +100 Per Cent. | +150 Per Cent. | +200 Per Cent. | −75 + 25 Per Cent. | −25 + 10 Per Cent. | −15+5 Per Cent. | −7 + 3 Per Cent. |
|---|---|---|---|---|---|---|---|
| Arthur Mill Concentrates | | | | | | | |
| Chalcopyrite | 65.0 | 60.75 | 64.8 | 61.0 | 58.9 | 72.0 | 78.7 |
| Bornite | 5.04 | 7.92 | 12.12 | 8.33 | 5.57 | 3.35 | 1.4 |
| Chalcocite | 20.65 | 22.65 | 14.8 | 18.3 | 17.7 | 13.25 | 8.47 |
| Covellite | 9.46 | 7.92 | 8.2 | 12.5 | 17.9 | 11.5 | 11.5 |
| Total | 100.15 | 99.24 | 99.92 | 100.13 | 100.07 | 100.10 | 100.07 |
| Arthur Mill Tailings | | | | | | | |
| Chalcopyrite | 43.7 | 58.0 | 47.0 | 54.1 | 49.25 | 48.7 | 41.25 |
| Bornite | 17.95 | 5.57 | 7.66 | 3.82 | 5.2 | 5.13 | 4.07 |
| Chalcocite | 33.8 | 33.2 | 42.2 | 26.1 | 26.9 | 23.0 | 31.4 |
| Covellite | 6.27 | 3.3 | 3.2 | 16.0 | 18.65 | 23.0 | 23.3 |
| Total | 100.72 | 100.07 | 100.06 | 99.02 | 100.00 | 99.83 | 100.02 |

[a] Table 7 in Report of 7/29/29.

[b] The sizes below 200 mesh are reported in terms of microns.

can undoubtedly be demonstrated and checked by experimentation in the laboratory.

The following items are noted as the outstanding features developed during the present study.

1. With the grinding practice in effect when the samples described in this study were produced (approximately 50 per cent. minus 200 mesh), the greater portion of the sulfide minerals are liberated. (See No. 5 for further explanation.)

2. From a standpoint of total copper represented mineralogically the minerals occur in the following sequence of importance: (a) chalcopyrite, (b) chalcocite, (c) covellite, and (d) bornite.

3. Better recovery of the chalcopyrite is being made than is the case with the other copper minerals.

4. The highest recoveries and the best grade of concentrates are made in the minus 200-mesh size. By separating the minus 200-mesh material into four size

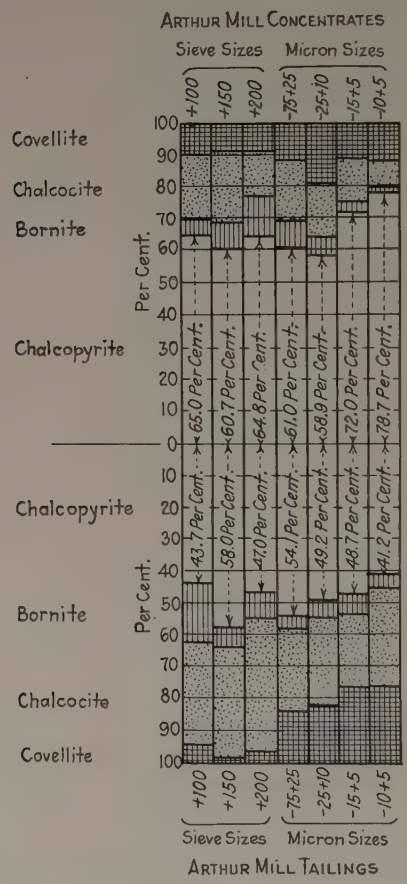



Fig. 2.—Percentage distribution of copper as mineralogically represented in concentrates and tailings.
Plotted from data given in Table 3.

classifications, the study shows a progressive increase in recovery beyond the minus 19 micron size (−800 mesh). The additional increase in grade and recovery are obviously subject to grinding costs and other practical and economic considerations.

4*a*. It is of interest to note that the elimination of pyrite is progressively better in the finer sizes.

5. The increased recoveries and generally favorable facts regarding fine grinding of the sulfides are probably due to the production of particles having fresh, untarnished

surfaces which are more readily floatable than those whose liberation alone has been accomplished.

6. Although the present report has resulted from intensive study the results tabulated suggest that further work of a like nature is necessary to make the survey complete. In this respect it appears that a study of primary slimes would be important since much of the copper content of this product may be represented by tarnished or partly oxidized sulfides together with strictly oxidized copper minerals. Separate treatment of the primary slimes might prove attractive and feasible from a mineralogical standpoint. The economics of such procedure have no doubt received consideration on the part of the operating department.

Criticism and comment on this report are invited.

TABLE 4.[a]—*Microscopic Determination of Distribution of Iron as Mineralogically Represented in Concentrates and Tailings from the Utah Copper Co. Composite Samples for a 30-day Period*[b]

| Minerals | +100 Per Cent. | +150 Per Cent. | +200 Per Cent. | −75 + 25 Per Cent. | −25 + 10 Per Cent. | −15+5 Per Cent. | −7 + 3 Per Cent. |
|---|---|---|---|---|---|---|---|
| Arthur Mill Concentrates | | | | | | | |
| Pyrite | 44.4 | 44.4 | 35.8 | 21.4 | 8.38 | 2.48 | 1.28 |
| Chalcopyrite | 54.2 | 53.3 | 60.45 | 75.2 | 88.8 | 96.2 | 98.0 |
| Bornite | 1.4 | 2.3 | 3.77 | 3.4 | 2.32 | 1.48 | 5.9 |
| Total | 100.00 | 100.00 | 100.02 | 100.00 | 99.50 | 100.16 | 99.87 |
| Arthur Mill Tailings | | | | | | | |
| Pyrite | 94.0 | 94.2 | 95.4 | 98.5 | 98.7 | 98.8 | 98.7 |
| Chalcopyrite | 5.2 | 5.63 | 4.45 | 1.64 | 1.26 | 1.1 | 1.3 |
| Bornite | 0.8 | 0.17 | 0.25 | 0.04 | 0.04 | 0.04 | 0.04 |
| Total | 100.00 | 100.00 | 100.10 | 100.18 | 100.00 | 99.94 | 100.04 |

[a] Table 8 in Report of 7/29/29.

[b] The sizes below 200 mesh are reported in terms of microns.

## CHEMICAL ANALYSES TO COMPLEMENT MICROSCOPIC STUDY

To check up and complement this microscopic report, chemical analyses of these same products were also made, and mesh recoveries calculated on total, sulfide and nonsulfide copper and sulfide iron. These results are shown in Tables 6, 7, 8, 9. Recovery of copper sulfide minerals as shown by chemical analysis checks the microscopic data and shows the amount of increase as the mineral particles become smaller, although for the chemical work no separation was made below 200 mesh. The calculated mesh recoveries of sulfide iron are likely to be misleading

unless interpreted by the microscopic analysis, for even the sulfide iron recovery increases with decrease in particle size. This is due to sulfide iron combined as chalcopyrite and bornite and not to increased pyrite recovery in the finer meshes. A study of both the microscopic and chemi-

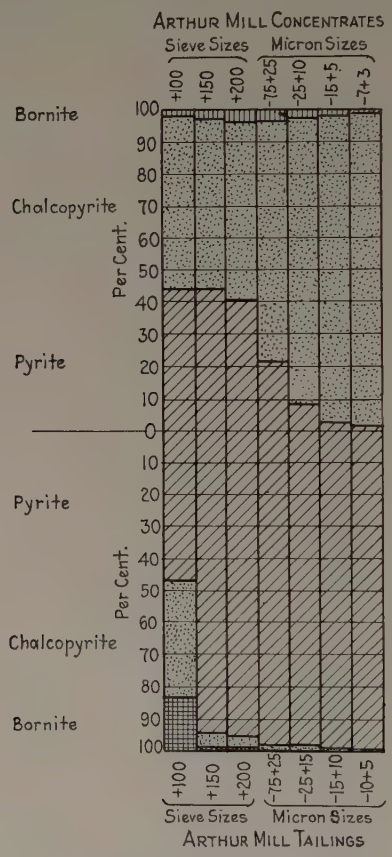



FIG. 3.—PERCENTAGE DISTRIBUTION OF IRON AS MINERALOGICALLY REPRESENTED IN CONCENTRATES AND TAILINGS.
Plotted from data given in Table 4.

cal analysis of the mesh products together with a knowledge of mill problems indicates the following conclusions:

1. If Utah Copper ore is ground to all through 100 mesh with ample classification, approximately 97 per cent. of the copper present as sulfide will be found in the −200 mesh. (See Table 10 for comparison of two degrees of grinding.) The microscope shows that little improvement in copper recovery can be made on mineral below the −200 and +25 micron

size; therefore to grind the flotation feed all through 100 mesh is probably as far as grinding can be economically carried.

2. Although pyrite rejection improves steadily even to the finest meshes, yet the increase in rejection as between the +25 micron size and the +3 micron size could not possibly pay for the cost of such grinding.

TABLE 5.[a]—*Summary Tabulation of Microscopic Determination of Sulfides, Sulfide Iron, and Sulfide Copper in Utah Copper Concentrates and Tailings*

Showing Weight Percentage Distribution of each Product by Recasting Total Per Cent of each Constituent in the Concentrate or Tailing to 100 Per Cent.

| Size Split | Pyrite | Chalcopyrite | Bornite | Chalcocite | Covellite | Sulfide | |
|---|---|---|---|---|---|---|---|
| | | | | | | Iron | Copper |
| **Arthur Mill Concentrates** | | | | | | | |
| Mesh | | | | | | | |
| +100 | 10.5 | 3.7 | 3.0 | 4.8 | 2.86 | 5.2 | 3.30 |
| +150 | 27.9 | 8.8 | 12.1 | 14.0 | 6.15 | 12.7 | 9.70 |
| +200 | 26.0 | 11.0 | 21.7 | 10.4 | 7.48 | 14.1 | 11.40 |
| Microns | | | | | | | |
| −75 + 25 | 26.3 | 24.2 | 35.7 | 30.0 | 26.71 | 24.9 | 26.50 |
| −25 + 10 | 6.3 | 17.6 | 17.5 | 21.9 | 28.81 | 15.3 | 19.90 |
| −10 + 5 | 1.08 | 11.2 | 5.5 | 8.5 | 9.61 | 9.0 | 10.35 |
| −7 + 3 | 0.86 | 17.1 | 3.3 | 7.6 | 13.51 | 13.6 | 14.60 |
| Settled between 20 min. and 30 hr. | 0.126 | 5.4 | 1.0 | 2.4 | 4.16 | 4.4 | 3.60 |
| Suspended after 30 hr. | 0.034 | 1.0 | 0.2 | 0.4 | 0.71 | 0.7 | 0.45 |
| Total | 100.000 | 100.0 | 100.0 | 100.0 | 100.00 | 100.9 | 99.80 |
| **Arthur Mill Tailings** | | | | | | | |
| Mesh | | | | | | | |
| +100 | 14.5 | 32.2 | 66.2 | 36.3 | 17.7 | 14.0 | 33.0 |
| +150 | 7.0 | 16.7 | 7.9 | 14.1 | 3.7 | 6.6 | 13.3 |
| +200 | 6.7 | 12.5 | 10.2 | 16.5 | 3.2 | 7.3 | 12.4 |
| Microns | | | | | | | |
| −75 + 25 | 6.7 | 4.5 | 1.6 | 3.2 | 5.0 | 11.9 | 3.8 |
| −25 + 15 | 8.2 | 4.2 | 1.7 | 3.2 | 6.1 | 7.7 | 4.1 |
| −15 + 10 | 14.7 | 6.6 | 3.1 | 4.7 | 12.5 | 13.6 | 6.4 |
| −10 + 5 | 21.0 | 12.0 | 4.6 | 12.5 | 25.8 | 19.5 | 13.3 |
| −5 (estimated) | 21.2 | 11.3 | 4.7 | 9.5 | 26.0 | 19.4 | 13.7 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] Table 9 in Report of 7/29/29.

3. Average Utah Copper ore at the present time contains copper sulfide minerals in about the following percentages:

| | Mineral in Ore, Per Cent. | Copper Content, Per Cent. |
|---|---|---|
| Chalcopyrite | 80 | 34.5 |
| Chalcocite | 9 | 79.8 |
| Covellite | 7 | 66.4 |
| Bornite | 4 | 63.3 |
| Average | | 41.96 |

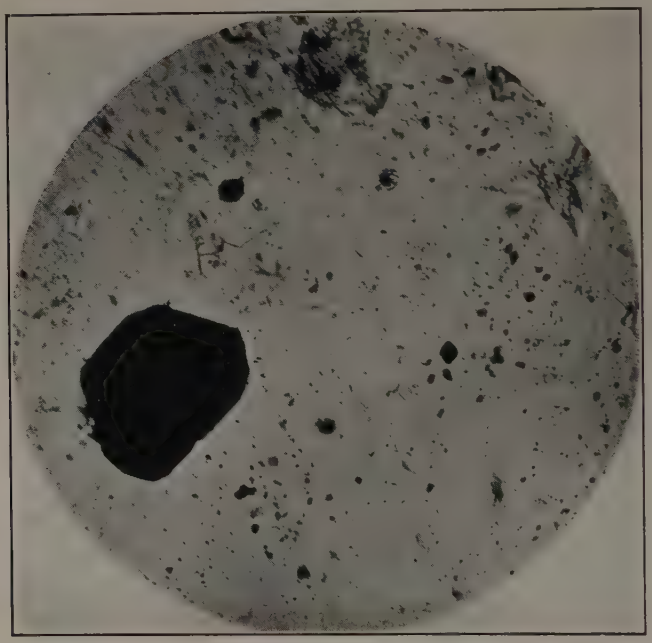


Fig. 4.—Disseminated sulfides in quartz-sericite gangue. × 165.
Portion of a quartz-sericite grain about 5 mm. dia. This grain was one of several random particles from the experimental heads of the Arthur plant briquetted in bakelite and ground to a thin section. The photomicrograph was taken with transmitted light and the sulfides, mostly pyrite, thus show as black specks in the transparent quartz-sericite gangue. The large black spot is a pyrite crystal slightly over 0.1 mm. ($100\mu$ or $-150$ mesh) in diameter; the next largest is under 0.02 mm. ($20\mu$) and many sulfide specks smaller than $5\mu$ can be seen readily.

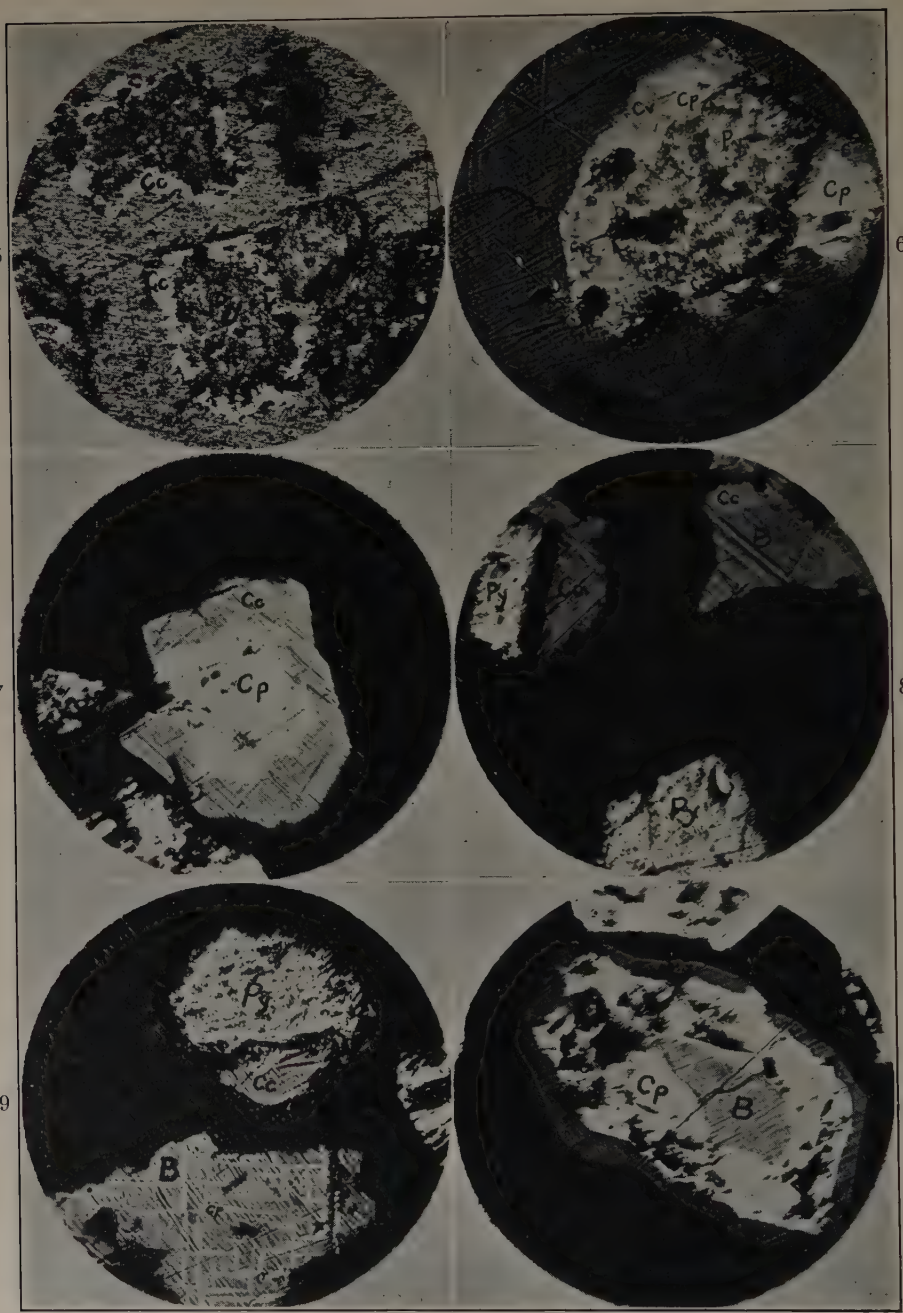
With about 9 per cent. of inert matter (insoluble and acid-soluble silicates) present, these minerals would give a concentrate of 38.19 per cent. copper, even though no pyrite whatever were floated. The mills have made 32 to 33 per cent. copper concentrate on similar ores with the feed ground only to 10 per cent. plus 100 mesh, hence the conclusion No. 2.

TABLE 6.—*Total Copper from 30-day Composites after Coarse Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Copper | | Material, Grams | Copper | | Material, Grams | Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.9841 | 98.40880 | 9,732.91 | 0.1807 | 17.58737 | 267.09 | 30.2600 | 80.82143 | +100 | 29.74 |
| +100 | 2,613.17 | 0.3894 | 10.17584 | 2,599.66 | 0.2750 | 7.14906 | 13.51 | 22.404 | 3.02678 | +150 | 80.21 |
| +150 | 1,016.09 | 0.9797 | 9.95440 | 984.97 | 0.2000 | 1.96994 | 31.12 | 25.657 | 7.98446 | +200 | 89.26 |
| +200 | 945.37 | 1 1216 | 10.60287 | 911.00 | 0.1250 | 1.13875 | 34.37 | 27.536 | 9.46412 | −200 | 89.17 |
| −200 | 5,425.37 | 1.2475 | 67.67898 | 5,237.28 | 0.1400 | 7.33219 | 188.09 | 32.084 | 60.34679 | Over-all | 82.13 |

TABLE 7.—*Sulfide Copper from 30-day Composites after Coarse Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Sulfide Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Sulfide Copper | | Material, Grams | Sulfide Copper | | Material, Grams | Sulfide Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.9319 | 93.18862 | 9,732.91 | 0.1338 | 13.02263 | 267.09 | 30.0146 | 80.16599 | +100 | 32.06 |
| +100 | 2,613.17 | 0.3587 | 9.37433 | 2,599.66 | 0.2450 | 6.36917 | 13.51 | 22.244 | 3.00516 | +150 | 81.72 |
| +150 | 1,016.09 | 0.9546 | 9.69984 | 984.97 | 0.1800 | 1.77295 | 31.12 | 25.472 | 7.92689 | +200 | 90.76 |
| +200 | 945.37 | 1.0950 | 10.35193 | 911.00 | 0.1050 | 0.95655 | 34.37 | 27.336 | 9.39538 | −200 | 93.84 |
| −200 | 5,425.37 | 1.1754 | 63.76691 | 5,237.28 | 0.0750 | 3.92796 | 188.09 | 31.814 | 59.83895 | Over-all | 86.03 |


5
Cc
Cc
6
Cv
Cp
P
Cp
7
Cc
Cp
8
Cc
B
Py
Cc
B
9
Py
Cc
B
10
Cp
B

4. It has been a belief of many flotation research men that pyrite if ground to very fine meshes floats readily and is hard to depress. These microscopic results prove that just the opposite is true so far as Utah Copper ore is concerned.

5. Separate sand and slime treatment offers a possibility of making a fair recovery of nonsulfide copper and much work has been done along this line. From 75 to 85 per cent. of the nonsulfide copper in this flotation feed is present in the −200-mesh size.

These conclusions are obviously almost in perfect agreement with the outstanding features noted by the microscopists.

Composite samples of tailings and concentrates are now being prepared with grinding averaging from 5 to 7 per cent. +100 mesh. These will be examined in the same manner as the previous samples, taken when grinding was poor, and comparisons will be made. Unfortunately, these results will not be available in time to present in this paper, but screening

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FIG. 5.—PYRITE CRYSTALS ENCASED IN THIN CHALCOCITE SHELLS. × 165.

Pyrite is dark because of being rough and unpolished. Chalcocite was polished smooth so that it reflected a large amount of light to the photographic plate and therefore appears light in the picture. Thin shells of chalcocite and covellite often occur surrounding pyrite grains in the + 100 and +150-mesh sizes but are difficult to show in a photograph owing to the great difference in the hardness of the minerals and to the fact that chalcocite and covellite, unless highly polished, appear similar to the bakelite matrix in a photograph. The chalcocite shell is from 10 to 25 microns. It is evident that pyrite grains coated as illustrated react with flotation reagents as though they were entirely chalcocite, and until the shell is removed by finer grinding a clean separation is impossible. These grains are from the +150-mesh Arthur concentrates.

FIG. 6.—PYRITE EMBEDDED IN CHALCOPYRITE AND COVELLITE. × 290.

From briquet of Arthur mill concentrates −100 mesh +150 mesh. Black spots are pits which did not reflect light to the photographic plate. The theory advanced in the description of Fig. 5 regarding floatability and liberation applies to grains of this character.

FIG. 7.—CHALCOPYRITE ENCASED IN CHALCOCITE. × 290.

From Arthur concentrate −100 mesh +150 mesh. Although this grain is composed of two minerals, liberation is not as important as with the pyrite-copper minerals shown in the preceding figures. This grain would have, presumably, the floatability of chalcocite, and finer grinding, liberating the constituent minerals, would be of advantage because under prevailing practice at the Utah Copper Co. plants, better recovery is made of chalcopyrite than of chalcocite.

FIG. 8.—A FREE PYRITE GRAIN, A PYRITE CUBE SURROUNDED BY CHALCOCITE. AND A GRAIN OF BORNITE-CHALCOCITE. × 290.

Area on surface of a briquet of Arthur concentrates −100 mesh +150 mesh. Shells of copper sulfides on pyrite grains are undoubtedly responsible for presence of some of the pyrite in the concentrates.

FIG. 9.—COMPLEX BORNITE-CHALCOPYRITE ASSOCIATION. × 290.

Bornite containing secondary chalcopyrite veinlets arranged along the crystallographic directions of the bornite. This illustrates the impossibility of securing complete liberation of copper minerals even by extremely fine grinding. In the pyrite-chalcocite middling grain the intergrowth is not so intimate and would be broken up by slightly finer grinding. Arthur concentrate −100 mesh +150 mesh.

FIG. 10.—BORNITE-CHALCOPYRITE-COVELLITE INTERGROWTH. × 290.

Particle from Arthur mill concentrates, −100 mesh +150 mesh. Center is core of bornite about 35 microns thick containing minute secondary veinlets of chalcopyrite, surrounded by rim of chalcopyrite about 30 microns thick, which in turn is encased in thin shell of covellite from 7 to 10 microns thick. Black spots are pits in surface of the minerals.

TABLE 8.—*Nonsulfide Copper from 30-day Composites after Coarse Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Nonsulfide Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Nonsulfide Copper | | Material, Grams | Nonsulfide Copper | | Material, Grams | Nonsulfide Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.0522 | 5.22044 | 9,732.91 | 0.0469 | 4.56473 | 267.09 | 0.2455 | 0.65571 | +100 | 2.70 |
| +100 | 2,613.17 | 0.0307 | 0.80152 | 2,599.66 | 0.0300 | 0.77990 | 13.51 | 0.1600 | 0.02162 | +150 | 22.62 |
| +150 | 1,016.09 | 0.0251 | 0.25456 | 984.97 | 0.0200 | 0.19699 | 31.12 | 0.1850 | 0.05757 | +200 | 27.39 |
| +200 | 945.37 | 0.0265 | 0.25094 | 911.00 | 0.0200 | 0.18220 | 34.37 | 0.200 | 0.06874 | −200 | 12.98 |
| −200 | 5,425.37 | 0.0721 | 3.91207 | 5,237.28 | 0.0650 | 3.40423 | 188.09 | 0.2700 | 0.50784 | Over-all | 12.56 |

TABLE 9.—*Sulfide Iron from 30-day Composites after Coarse Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Sulfide Iron Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Iron as Sulfide | | Material, Grams | Iron as Sulfide | | Material, Grams | Iron as Sulfide | | Mesh | Recovery |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 1.8013 | 180.13018 | 9,732.91 | 1.123 | 109.30058 | 267.09 | 26.519 | 70.82960 | +100 | 13.70 |
| +100 | 2,613.17 | 0.9914 | 25.90751 | 2,599.66 | 0.860 | 22.35708 | 13.51 | 26.280 | 3.55043 | +150 | 36.53 |
| +150 | 1,016.09 | 2.3519 | 23.89770 | 984.97 | 1.540 | 15.16854 | 31.12 | 28.050 | 8.72916 | +200 | 40.54 |
| +200 | 945.37 | 2.5120 | 23.74754 | 911.00 | 1.550 | 14.12050 | 34.37 | 28.010 | 9.62704 | −200 | 45.92 |
| −200 | 5,425.37 | 1.9636 | 106.53229 | 5,237.28 | 1.100 | 57.61008 | 188.09 | 26.010 | 48.92221 | Over-all | 39.32 |

TABLE 10.—*Flotation Feed, 30-day Composite, Utah Copper Co. Arthur Plant*

| Mesh | Material | | | Copper | | |
|---|---|---|---|---|---|---|
| | Grams | Per Cent. | Accum., Per Cent. | Per Cent. | Per Cent. Weight | Accum., Per Cent. Weight |
| Actual Mill Grinding, No. 1 | | | | | | |
| Original | 660.0 | | | 0.970 | | |
| +100 | 54.6 | 8.27 | 8.27 | 0.188 | 1.61 | 1.61 |
| +150 | 72.3 | 10.95 | 19.22 | 0.300 | 3.39 | 5.00 |
| +200 | 61.5 | 9.31 | 28.53 | 0.645 | 6.19 | 11.19 |
| −200 | 471.6 | 71.47 | 100.00 | 1.205 | 88.81 | 100.00 |
| Cut of Same Heading, After Regrinding 5 Min. in Laboratory Ball Mill No. 2 | | | | | | |
| | 500.00 | | | 0.960 | | |
| +100 | 9.0 | 1.80 | 1.80 | 0.160 | 0.30 | 0.30 |
| +150 | 24.3 | 4.86 | 6.66 | 0.200 | 1.01 | 1.31 |
| +200 | 39.4 | 7.88 | 14.54 | 0.420 | 3.45 | 4.76 |
| −200 | 427.3 | 85.46 | 100.00 | 1.070 | 95.24 | 100.00 |

Calculated total copper recovery, Grind No. 1, 90.836 per cent.; Grind No. 2 92.463 per cent.

and chemical analyses of 30-day composite samples from feed averaging 9.60 per cent. +100-mesh material have been made and are given in Tables 11, 12 and 13.

The two runs of ore covered by Tables 6, 7, 8 and 9 and by Tables 11, 12 and 13 are almost alike in nonsulfide copper content, and both are about average for Utah Copper ore during the past year or more. On account of the very low recovery of nonsulfide copper, any increase of nonsulfide in the heading means a certain increase in tailing loss. In addition to this, sulfide copper recovery also decreases with ores high in nonsulfide. A comparison of these two sets of tables shows the decided improvement in metallurgy on the later run, total copper recovery having increased from 82.13 to 90.67 per cent. and the grade of concentrate increasing from 30.26 to 31.95 per cent. It may be noted that the percentage of recoveries on the +100, +150 and +200 meshes have decreased with finer grinding, even though the tailing mesh assays are lower. This is due entirely to the fact that these meshes in the heading assay are so much lower than with coarse grinding. The coarse grinding was done with an average daily tonnage of 27,643 and before any new grinding equipment was in operation. The fine grinding is from an average daily tonnage of 24,017 with all the new grinding and classifying equipment installed. That the new equipment has done all that was expected in

TABLE 11.—*Total Copper from 30-day Composites after Fine Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Copper | | Material, Grams | Copper | | Material, Grams | Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.9841 | 98.41085 | 9,720.71 | 0.0945 | 9.18607 | 279.29 | 31.947 | 89.22478 | +100 | 28.65 |
| +100 | 960.09 | 0.1969 | 1.89026 | 956.52 | 0.1410 | 1.34869 | 3.57 | 15.170 | 0.54157 | +150 | 65.18 |
| +150 | 1,104.94 | 0.2707 | 2.99131 | 1,096.50 | 0.0950 | 1.04167 | 8.44 | 23.100 | 1.94964 | +200 | 88.57 |
| +200 | 1,085.74 | 0.6841 | 7.42794 | 1,061.50 | 0.0800 | 0.84920 | 24.24 | 27.140 | 6.57874 | −200 | 93.09 |
| −200 | 6,849.23 | 1.2571 | 86.10016 | 6,606.19 | 0.0900 | 5.94557 | 243.04 | 32.980 | 80.15459 | Over-all | 90.67 |

TABLE 12.—*Sulfide Copper from 30-day Composites after Fine Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Sulfide Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Sulfide Copper | | Material, Grams | Sulfide Copper | | Material, Grams | Sulfide Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.9332 | 93.31894 | 9,720.71 | 0.0512 | 4.97700 | 279.29 | 31.6309 | 88.34194 | +100 | 32.91 |
| +100 | 960.09 | 0.1693 | 1.62539 | 956.52 | 0.1140 | 1.09043 | 3.57 | 14.9850 | 0.53496 | +150 | 73.06 |
| +150 | 1,104.94 | 0.2395 | 2.64591 | 1,096.50 | 0.0650 | 0.71273 | 8.44 | 22.9050 | 1.93318 | +200 | 92.47 |
| +200 | 1,085.74 | 0.6495 | 7.05252 | 1,061.50 | 0.0500 | 0.53075 | 24.24 | 26.9050 | 6.52177 | −200 | 96.78 |
| −200 | 6,849.23 | 1.1971 | 81.99504 | 6,606.19 | 0.0400 | 2.64248 | 243.04 | 32.650 | 79.35256 | Over-all | 94.67 |

TABLE 13.—*Nonsulfide Copper from 30-day Composites after Fine Grinding, Utah Copper Co. Arthur Plant*

| Mesh | Calculated Heading | | | Actual Tailing | | | Actual Concentrate | | | Nonsulfide Copper Recovered | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Material, Grams | Nonsulfide Copper | | Material, Grams | Nonsulfide Copper | | Material, Grams | Nonsulfide Copper | | Mesh | Recovery, Per Cent. |
| | | Per Cent. | Grams | | Per Cent. | Grams | | Per Cent. | Grams | | |
| Original | 10,000.00 | 0.0509 | 5.09191 | 9,720.71 | 0.0433 | 4.20907 | 279.29 | 0.3161 | 0.88284 | +100 | 2.49 |
| +100 | 960.09 | 0.0276 | 0.26486 | 956.52 | 0.0270 | 0.25826 | 2.57 | 0.1850 | 0.00660 | +150 | 4.77 |
| +150 | 1,104.94 | 0.0313 | 0.34541 | 1,096.50 | 0.0300 | 0.32895 | 8.44 | 0.1950 | 0.01646 | +200 | 15.17 |
| +200 | 1,085.74 | 0.0346 | 0.37541 | 1,061.50 | 0.0300 | 0.31845 | 24.24 | 0.2350 | 0.05696 | −200 | 19.54 |
| −200 | 6,849.23 | 0.0599 | 4.10512 | 6,606.19 | 0.0500 | 3.30309 | 243.04 | 0.3300 | 0.80203 | Over-all | 17.34 |

the way of better metallurgy is evident. That still more grinding and classification will be profitable is also indicated by the microscopic work and by the example used in Table 10, for an increase of 1.6 per cent. in total copper recovery gives a fairly large margin of additional profit to work with.

There still remains to be made a microscopic study of gold and silver, but this will be difficult on account of the very minute quantities in average heading and tailing. During the test period when iron was first being rejected, the recoveries of gold and silver were checked against machines floating all the pyrite. Silver recovery apparently was not affected at all, going up and down in proportion to the copper recovery, and gold recovery dropped slightly. Actual mill results since that time have confirmed the fact that silver recovery has been high with high copper recovery and low with low copper recovery. Some of the gold in Utah Copper ore is free at coarse meshes, and was frequently visible on the Wilfley tables until the tables were discarded. Some gold, however, is closely associated with the pyrite and is carried into the tailings with it unless the pyrite is ground to the finer meshes. With coarse flotation feed, pyrite has been refloated out of the mill tailings, and when assayed was found to contain 0.025 oz. gold per ton. Even at that time, the total gold recovery had only decreased 2 to 3 per cent. over what it was when part of the gold was removed on tables and all the pyrite was floated. It is expected, therefore, that with feed ground to 85 per cent. −200-mesh, gold recovery will be practically as high as though all the pyrite were floated. Silver recovery has not suffered at all through rejection of pyrite.

## Summary

Careful microscopic examination of mill products has been an invaluable aid to the metallurgical staff at the Utah Copper mills in pointing out possible improvements in metallurgy. All of the early microscopic data were made available by the cooperation of U. S. Bureau of Mines Experiment Station at Salt Lake. Later, when the volume of work increased beyond the point where it could be handled by a one-man laboratory, various companies, together with the Bureau of Mines, equipped and are helping to support a new cooperative microscopic laboratory. This makes possible much more exhaustive investigations than were undertaken previously. Careful chemical work, together with actual mill results, have proved the microscopic data correct in practically every case. Further microscopic work will be necessary from time to time because ores in the Utah Copper mine vary widely in characteristics and mineral content.

# DISCUSSION

O. C. Ralston, Clarkdale, Ariz.—At the United Verde Copper Co. we have been doing the same thing for the past year and a half. We have installed an ore-dressing microscopist. When we are grinding everything for flotation, it is almost impossible to tell anything about mineral losses or dilution of concentrate by ordinary visual inspection, and while a mill is in operation, the daily assays, if they are wrong or embarrassing in any way, can be explained away by the mill operatives by many fanciful hypotheses—bad ore, locked mineral, dissolved salts, any number of alibis—and it is really almost necessary to, you might say, check up on mill operatives by having someone with a microscope actually look at the material and see if any of these possible explanations are correct.

It is impossible to tell much by simply putting ground material under the microscope. Specimens must be prepared. We started by embedding specimens in wax, the so-called "chaser" wax that the Geological Survey uses for making sections of granular materials, but this wax was not good for such a preparation because for material under 200 mesh the preparation came out full of bubbles. When a polished section was made through such a briquette, there were too many pits caused by the bubbles.

We have adopted a powdered bakelite as a binder, curing the bakelite in an electrically heated press, taking from 10 to 15 min. to prepare a briquette. When a slice is taken through, there is an opportunity to see what each grain really has in it, because the polished section shows a great many things, especially the presence of locked mineral grains.

The microscopist reports the approximate percentages of each mineral that is present as locked mineral grains or as visibly locked mineral grains. In taking a cross-section through a mineral grain, it may be that the invisible part of the grain consists of something else and any one mineral grain may have any number of other things attached to it in the invisible, buried portion.

However, for ordinary grinding the size necessary for liberation is being approached and the usual locked mineral grain will contain only two minerals. If the *average* locked mineral grain is one-half of one mineral and one-half of the other, with a plane interface between the two, we might in making the cross-section pass the plane of cutting parallel to that interface, or at either of the two sets of planes perpendicular to it. All of the planes paralleling that interface will show only one mineral. All of the two sets of planes perpendicular to that interface show two minerals in the grain. Therefore, roughly, the probability is that for every two grains that are visibly locked, there is a third one which is not visibly locked; consequently, the microscopist's estimate of, say, 10 per cent. *visibly* locked chalcopyrite must be corrected to 15 per cent., probably locked chalcopyrite. The same reasoning can be extended to planes not parallel or perpendicular to the interface.

By frequent examinations of briquetted materials, concentrate, tailing, various intermediate products, it is astounding to find, for instance, a concentrate loaded with rejectable pyrite, or to find a tailing containing too much recoverable mineral; the diagnosis then is that it is a poor flotation condition. The cause of the condition must be sought elsewhere, but at least more of the truth can be learned of what is going on in the flotation mill.

The grinding problem at Clarkdale is a serious one. The massive sulfide ore requires about 800-mesh grinding for 90 per cent. liberation of the desired minerals, and of course that is at present commercially impossible. It is necessary to separate the sizes of material actually obtainable and study them separately to see how much liberation can be obtained with different grinds and to accept the best compromise indicated by that study. Therefore, the microscopic laboratory needs not only the

briquetting press but an elutriation apparatus to separate fines, as no screens can be had finer than about 300 mesh. In our case, with a massive sulfide ore, elutriation is entirely satisfactory; we make cuts at the equivalent of 400-mesh, 800-mesh, and occasionally 1600-mesh sizes, to be separately briquetted, polished and studied by the microscope.

C. E. Locke, Cambridge, Mass.—What pressure do you put on the briquette?

O. C. Ralston.—The briquetting press is a small home-made steel spool wound with resistance wire, making a cylindrical briquette about 1 in. dia., perhaps ¼ in. thick, and the pressure is put on by a hydraulic jack of 1½ tons total capacity. We never exert the whole pressure on the ¾-in. sq. cross-section. Probably one ton is actually exerted.

C. E. Locke.—It was my impression that Professor Gaudin now goes up to practically 2 tons pressure in some of his briquette work. That point is very interesting in showing that what appears to be a minor detail really becomes an important factor in the development of certain lines of investigation. Originally in doing microscopic work we thought all we had to do was to mix up the ground material with some sort of wax and then polish it. We have found that it is not so easy, and that a great deal of technique must be developed.

# Selectivity Index; a Yardstick of the Segregation Accomplished by Concentrating Operations

By A. M. Gaudin,* Butte, Mont.

(New York Meeting, February, 1930)

Direct quantitative comparison of the results of concentrating operations on different ores is frequently desired but almost impossible to obtain if comparison has to be made by means of two quantities for each ore, as must be done at present. This paper represents the outgrowth of attempts to arrive at a *single-number* quantitative measure of the segregation between minerals or metals as the result of concentrating operations.

The usual practice in estimating the effectiveness of concentrating operations, particularly those of ore dressing, has been to determine the recovery of the metal or mineral of interest and the grade of the concentrate. The difficulty in quantifying the effectiveness of concentration by the usual criteria may be illustrated by a few examples. Consider, for instance, two lead ores which yield by flotation the same recovery of lead, say 92 per cent., and the same grade of concentrate, say 60 per cent. Pb. If a substantial difference in the grade of the feed had existed, say if one ore contained 5 per cent. Pb and the other 10 per cent., it is clear that the concentrating operation was more effective in the case of the lower grade ore. It is difficult, however, in the light of these data to state how much more effective was the concentration of the lower grade ore. Consider again two lead ores containing 5 and 10 per cent. Pb and yielding concentrates containing 60 and 72 per cent. Pb respectively, with recoveries of 93 and 92 per cent. respectively; it is well-nigh impossible to tell from these figures which results represent the best separation of the minerals. It may be noted that in the usual method of estimating the effectiveness of the segregation of mineral values, no consideration is given to the rejection of the unwanted substances from the concentrate, except in the very indirect manner in which it enters into the grade of the concentrate. Consideration of the rejection of gangue from the concentrate, adequately weighted with recovery of the desired mineral in the concentrate, should supply an adequate criterion of concentration effectiveness.

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* Research Professor of Ore Dressing, Montana School of Mines.

## Indices in Use

In gaging the work done at the Sullivan Concentrator of the Consolidated Mining and Smelting Co. of Canada, R. W. Diamond[1] has been using an index known as "metallurgical efficiency" which embodies the requirement of considering the rejection of the unwanted minerals from the concentrate. As applied to the Kimberley ore, it is obtained by adding the recovery of the lead in the lead concentrate to that of the zinc in the zinc concentrate and to that of the iron in the tailing, then dividing the sum by 3. The nearer this average is to 100, the more perfect is the metallurgical efficiency.

A somewhat similar index called "coefficient of perfection" was used for two years in the author's laboratory.[2] This number is obtained by adding the recovery of one of the minerals or metals in the concentrate to the recovery of the other metal or mineral in the tailing and subtracting 100 from the sum. The larger the coefficient of perfection, the better the separation. This coefficient of perfection is similar to Diamond's metallurgical efficiency but it is always numerically smaller; in other words, it places added emphasis on the removal of the last traces of impurity in a segregated product.

The disadvantage of both the metallurgical efficiency and coefficient of perfection is that the improvement in the work that results from small increases in the indices when these approximate 100 does not receive adequate recognition. For instance, a coefficient of perfection of 98 represents work vastly better than a coefficient of perfection of 96, although, when expressed as a coefficient of perfection, the improvement seems to be of the order of 2 per cent. It is to overcome this defect that a new index was developed, which has been called the selectivity index.

## Selectivity Index

In order to arrive at a simple definition of the selectivity index it is perhaps easiest to consider an example. Let it be assumed, as above, that 92 per cent. of the total lead in an ore is recovered in the concentrate by flotation, and that the rejection of the gangue is 95 per cent. Clearly the recovery of the gangue is 5 per cent., so that the floatability of the lead is $9\frac{2}{5}$ times as great as that of the gangue, since it is recoverable to an extent $9\frac{2}{5}$ times as large. This ratio $9\frac{2}{5}$ is then a measure of the relative floatability of the lead minerals and the gangue minerals. Similarly, the rejection of gangue is 95 per cent. and the rejection (or loss) of lead is 8 per cent., so that the relative rejectability of gangue and

[1] R. W. Diamond: Ore Concentration Practice of the Consolidated Mining and Smelting Co. of Canada, Ltd. Flotation Practice, A. I. M. E. (1928) 102.

[2] A. M. Gaudin, H. Glover, M. S. Hansen and C. W. Orr: Flotation Fundamentals, I. Utah Eng. Expt. Sta. *Tech. Pub.* 1 (1928).

lead is $^{95}/_{8}$. The relative floatability and the relative rejectability of the mineral and the gangue should be considered as equally important in bringing about the segregation of the minerals: some average between these numbers should therefore constitute an adequate yardstick to measure the quality of the segregation obtained.

Before proceeding to the determination of how the average between the relative floatability and the relative rejectability of the two substances should be struck, it might be of interest to note that the ratio between the recovery and rejection of each substance has some definite significance: it may be construed to represent a measure of the recoverability of the substance. In the above instance the recoverability of the lead is $^{92}/_{8}$; that of the gangue is $^{5}/_{95}$. The ratio of the recoverability of the galena to the recoverability of the gangue is a measure of the segregation of the lead and gangue into concentrate and tailing.

Of the various averages that can be calculated, the arithmetical and the geometrical average appear to have the widest application and justification in the field of the natural sciences. In this instance, a geometrical average in place of an arithmetical one prevents undue weight being placed on one of the ratios, which would lead to a warped estimation of the effectiveness of the segregation if one of the factors were much larger than the other; also, it leads to a factor that is identical with the ratio of the recoverability of one mineral to that of the other. Thus, in the example taken above, the selectivity index calculated by one method becomes $\sqrt{(^{92}/_{5}) \times (^{95}/_{8})}$, and by the other method $\sqrt{\frac{(^{92}/_{8})}{(^{5}/_{95})}}$. These two averages are identical.

## Calculating Selectivity Index

In calculating the selectivity index the easiest way would appear to consist of the following steps:

1. Calculate the recovery, $x$, of any one certain metal or mineral; the rejection of that metal or mineral is $100 - x$; the ratio $x/(100 - x)$ is the first term to be averaged.

2. Calculate the rejection, $y$, of any one certain metal or mineral; the recovery of that metal or mineral is $100 - y$; the ratio $y/(100 - y)$ is the second term to be averaged with the first.

3. The square root of the product of $x/(100 - x)$ and $y/(100 - y)$ is the selectivity index sought.

The selectivity index has been in use at the author's laboratory for about one year and during this time has become thoroughly tested as to its applications. It has been found to have wider use than was anticipated at first, because of allowing a direct comparison between the work at various mills treating different kinds of ore, or between mills treating ores containing different proportions of the same minerals. It has thus

been possible to establish the average relative floatabilities of galena to sphalerite in practice over a wide range of natural conditions. Such a comparison would have been totally impossible without the use of such an index as was devised. The use of the selectivity index also allows comparison of the effectiveness of flotation reagents from mill to mill.

TABLE 1.—*Selectivity Indices in Sulfide Lead-zinc Plants*

| Plant No. | Year | Lead Cycle | | | Zinc Cycle | |
|---|---|---|---|---|---|---|
| | | Lead-zinc | Lead-iron | Lead-nonsulfide Gangue | Zinc-iron | Zinc-nonsulfide Gangue |
| 1 | 1926 | 2.3 | —— | 19.4 | —— | —— |
| 2 | 1926 | 5.8 | 15.6 | 22.4 | —— | 20.5 |
| 3 | 1925 | 9.6 | 10.8 | 77.1 | 7.5 | 29.5 |
| 4 | 1925 | 4.0 | —— | —— | | —— |
| 5 | 1928 | 14.2 | 15.9 | 34.8 | 17.7 | 21.7 |
| 6 | 1929 | 10.9 | 14.3 | 73.0 | 7.6 | 26.9 |
| 7 | 1929 | 9.7 | 19.4 | —— | 14.9 | —— |
| 8 | 1928 | 9.0 | 18.5 | 53.2 | 16.0 | 58.0 |
| 9 | 1928 | 6.9 | 13.1 | 28.7 | 8.8 | 24.0 |
| 10 | 1927 | 6.8 | —— | —— | | —— |
| Geometric averages..... | | 7.1 | 15.1 | 39.0 | 11.1 | 28.2 |

TABLE 2.—*Geometric Averages of Selectivity Indices in Selective Flotation Plants*

| Kind of Ore | Number of Plants | Cycle | Selectivity Index | Numerical Value of Selectivity Index |
|---|---|---|---|---|
| Free-milling sulfide lead-zinc ore. | 2 | Lead | Lead-zinc | 15.9 |
| Complex sulfide lead-zinc ores... | 10 | Lead | Lead-zinc | 7.1 |
| | 7 | Lead | Lead-iron | 15.1 |
| | 7 | Lead | Lead-nonsulfide gangue | 39.0 |
| | 6 | Zinc | Zinc-iron | 11.1 |
| | 6 | Zinc | Zinc-nonsulfide gangue | 28.2 |
| Oxidized lead-silver ores..... | 5 | Lead | Lead-all gangue | 10. |
| | 1 | Lead | Lead-insol. | 13.3 |
| | 1 | Lead | Lead-lime | 4.2 |
| | 1 | Lead | Lead-iron | 8.4 |

Its usefulness would seem to transcend its applications in flotation, and in other branches of ore dressing; there seems to be no reason why it should not apply equally well in other metallurgical operations such as smelting, roasting, and refining. In ore dressing it would be preferable to determine the selectivity indices in terms of minerals rather than in

terms of metals, as the units there are mineralogical; in metallurgical operations it may be desirable, on the other hand, to express selectivity indices as between elements rather than compounds.

Table 1 presents the results obtained in various Western plants treating by flotation complex sulfide lead-zinc ores; Table 2 presents the geometrical averages of several selectivity indices in a number of flotation plants treating different types of ores. Table 1 shows that in the lead-floating cycle of selective flotation plants the lead-zinc selectivity index is smaller than the lead-iron index and that the lead-nonsulfide gangue index is much larger than either. Table 2 gives a quantitative notion of the relative ease of separation of various minerals by flotation.

It is not suggested that the selectivity index should replacethe usual criteria employed in ore dressing; it is merely believed that it will prove to be a useful adjunct to our present criteria. Comments and criticism would be highly appreciated.

# Cyanide Regeneration or Recovery as Practiced by the Compania Beneficiadora de Pachuca, Mexico

By C. W. Lawr,* Pachuca, Hidalgo, Mexico

(San Francisco Meeting, October, 1929)

The ores mined by the Santa Gertrudis Co. at Pachuca, Mexico, are mainly silver-bearing; they also yield some gold and carry a little copper. Strong cyanide solutions are used to dissolve the silver and gold, and the mechanical loss of cyanide at the tailings filter has been considerable. Prior to the year 1923, the pulp, after agitation, was given a 35 to 37-min. wash with barren solution in a Butters-type leaf filter; the discharged slime cake was repulped and pumped into eight Merrill self-sluicing slime presses in which the slime was given a further wash with barren solution for 25 to 35 min., followed by a 10-min. water wash.

At that time the barren solution titrated around 0.350 per cent. free KCN and 0.500 per cent. total KCN. (Aero brand cyanide is used.) It can readily be seen that a 10-min. water wash would leave considerable cyanide in the filter cake, which of course was a total loss. This averaged 0.522 kg. (1.15 lb.) KCN per ton of solution. As the daily discharge to the dam was 1600 tons[1] of slime of a 2:1 ratio of liquid to solid, the value of this mechanical loss of cyanide was an important item and its recovery held alluring possibilities.

## Principle of Cyanide-recovery Process

As it had acquired the patent rights to the Layng (H. R.) and Halvorsen (A. L.) processes, also those of Mills (L. D.) and Crowe (T. B.) after considerable experimental work in its own laboratory and at Tonopah, Nev., The Merrill Company of San Francisco early in 1923 notified the Mexican Corporation and Compania de Santa Gertrudis of its process for the recovery of cyanide from weak wash solutions, or for the transference of cyanide from a foul mill solution to a clean alkaline solution. This method is known as the Mills-Crowe process, the principle of which is as follows:

The solution from which the cyanide is to be removed is made acid by bringing it into contact with sulfur dioxide ($SO_2$). The acidified solution is then transferred to a closed tank in which air and solution are brought into intimate contact. The air leaving the tank charged with HCN is then passed to another tank in which it is mixed with an alkaline solution,

* Metallurgist, Cia. Beneficiadora de Pachuca (subsidiary of Santa Gertrudis Co.).

[1] Metric ton of 2204 lb. used in this paper.

the latter absorbing the HCN and leaving the accompanying air clean for reuse in removing more HCN from the acidified solution.

The extent to which the acidified solution will become impoverished of its cyanide will depend upon the acidity, the amount of air brought into contact with the solution, and the quantity of residual HCN left in the air after the latter has passed the absorbing apparatus. (The system is closed so that the same air is used over and over again.)

Of course the amount of air required will depend on how efficiently it is utilized, but where the other conditions are equal it may be stated that the amount of cyanide removed from a given volume of solution increases with an increase of air, and further, an increase of air will do more good, or a decrease will cause poorer results than almost any other change that could be made in the plant. (By increase of air is meant an increase in the velocity of that being circulated.)

The impoverished acid solution may be wasted or used as a water wash on the filters, either before or after filtering, depending on whether the solution contains sufficient silver or copper to pay for its removal. If the spent solution does not contain any silver, but much copper, it is doubtful if it could be used as a filter wash before filtering, because the slimy nature of the precipitate would adversely affect the filter leaching rate. However, this is one of the problems that still has to be worked out.

## First Attempts at Cyanide Recovery

As the recoverable cyanide losses were mainly mechanical and as the plant had plenty of filtering capacity, it appeared logical to wash with barren solution at the Butters filter only, discharge the washed cake to the Merrill filters and there wash with water only. This wash-water period would be equivalent to that for the previous combined periods of barren solution and water wash, if this should be found necessary. Of the wash-water effluent from the Merrill filters the first portion would be returned as make-up solution to the cyanide-plant circuit, while the remainder would go as solution feed to the cyanide-recovery plant. Any silver and gold precipitated out in the recovery plant would be recovered by filtration in a Butters clarifier, the precipitate returning to the agitators or thickeners (the entire amount of precipitate so produced is now removed by settlement and filtration and shipped to the smelter, none being returned to the cyanide circuit), and the clarified acid solution going to the Merrill filters as water wash.

With this possibility in view, an experimental recovery unit was installed, consisting of a vertical pipe 9 ft. high and 12 in. dia. to serve as an acidifier; 12 large steel oil drums connected in series, six as dispersers and six as absorbers; a blower, and a sulfur burner.

Although important data were obtained from this unit, many mechanical and chemical troubles were encountered. Of the former correct

submergence of the dispersers and absorbers was one, but this system was given up in favor of a complete tower system as used at the Fresnillo experimental recovery plant of the company in Zacatecas. The chemical trouble then started in the form of liming up of the tower and its discharge lines due to the high lime content of the solution being treated. This prevented the carrying out of a continuous test. However, as there were no such difficulties encountered in the experimental plant at Fresnillo, S. B. McCluskey, metallurgist there, determined that a 96 per cent. extraction of the total KCN might be expected with a consumption of 1.3 kg. (2.9 lb.) of sulfur per ton of solution treated, when using 15 cu. ft. of air per minute per ton of solution per 24 hr. Barren mill solution titrating 0.230 per cent. free KCN and 0.260 per cent. total KCN, and 0.048 per cent. CaO as protective alkalinity was being treated.

### *Filter Tests for Economical Washing Period*

As the experimental work at Fresnillo was so successful, the data obtained there were used at Pachuca as a basis upon which to design a plant capable of treating the required amount of solution from the Santa Gertrudis mill daily.

As our scheme required the treatment of a filter-wash effluent it was necessary to make a series of plant-scale tests on the Merrill filters in order to determine the most economical washing period, the amount of wash effluent that could be returned to the cyanide circuit, and the amount of solution that it would be necessary to treat in the recovery plant, with its average cyanide, lime and silver contents.

These tests were made by M. S. Booth, assistant mill superintendent. He found that the total wash water required to give the most economical extraction of the cyanide (at the time the tests were made) would be 22 tons for each 15 tons of dry ore in the filter press. The first 8 tons of the 22 tons would be returned to the cyanide circuit as make-up solution and the remaining 14 tons would go to the recovery plant for treatment.

The average analysis of the recovery-plant feed, as indicated by his tests, would be 0.079 per cent. free KCN; 0.103 per cent. total KCN; 0.057 per cent. CaO as protective alkalinity, and a methyl-orange titration giving an equivalent of 0.073 per cent. CaO; and a silver content of 1.8 g. per ton.

The amount of solution to be treated was 0.93 ton per ton of ore, and the entire amount of wash was equivalent to 3 tons per ton of caking effluent left in the filter cake as moisture after caking. Other pertinent data were also determined.

## Erection of Large-scale Cyanide-recovery Plant

Enough information was now available to design a cyanide-recovery plant capable of treating a minimum of 1400 tons and a maximum of 2000

tons of solution in 24 hr. This was done; the equipment was ordered from the United States in July, 1924, and at the end of March, 1925, it started operating on an 1800-ton basis. The nomenclature used in the cyanide-recovery plant is as follows:

*Nomenclature Used*

*Acidifier.*—The acidifier, as the name implies, is a tank, tower, or other receptacle in which the solution to be treated is first acidified by means of $SO_2$.

FIG. 1.—CYANIDE-RECOVERY PLANT OF COMPANIA BENEFICIADORA DE PACHUCA.

*Disperser.*—The disperser, or de-cyaniding tank, is a tall closed tank in which the cyanide in the form of HCN is removed by means of circulating air through the acidified solution coming from the acidifier.

*Absorber.*—The absorber is a closed tank similar in every respect to the disperser, as used by us, (but it may be of radically differing types), in which the HCN gas driven off from the disperser is absorbed in an alkaline solution. The absorbing solution may be any alkaline solution such as the ordinary mill cyanide solution, milk of lime, or sodium carbonate solution. The only requirement is that it should contain sufficient alkali to fix the cyanogen and still contain a generous amount to prevent dispersion in the absorbers. The quantity of absorbing solution necessary will depend on its alkali content and the efficiency with which it is brought into contact with the HCN.

*Clarifier.*—At Santa Gertrudis the Merrill water-wash effluent being treated in the recovery plant contains sufficient silver to make it worth saving. If the solution discharged from the last disperser contains enough free $SO_2$ and has been sufficiently dispersed, the copper and silver, when present, will precipitate completely. It will then only be necessary to remove the precipitate from the acid solution. For this purpose we converted a 35-ft. Dorr thickener into a filter tank containing sixty-six 5 by 11-ft. Butters type leaves. This filter is known as the recovery-plant clarifier.

## Description of Plant

Fig. 1 is a view and Fig. 2 shows the general arrangement and flow sheet of the cyanide-recovery plant. As stated elsewhere, the process consists of acidification as the first stage; followed by dispersion or the driving off of the HCN from the acidified solution, and the subsequent absorption of the HCN in an alkaline mill solution; with the possible removal of precipitated silver or copper or both, either by settlement or filtration.

### *Acidification*

Before the cyanogen can be efficiently removed in the form of HCN from the solution to be treated, the latter must have its alkaline constituents neutralized by some acid. Furthermore, in order to obtain the desired results without too great an expenditure for air, and too many dispersions, it has been our experience that a certain amount of acid must be present during dispersion. The acid must be either in the free state or in the form of bisulfites which will break down during the dispersion to form normal sulfites with the liberation of free $SO_2$. This is, of course, assuming that acidification is accomplished by means of $SO_2$.

The alkaline compounds that have to be neutralized are the alkaline cyanide itself, sodium hydrate, calcium hydrate, and possibly some calcium carbonate in suspension. The chlorides will also take up sulfur, but as its equivalent in hydrochloric acid will be liberated, chlorides do not actually destroy or consume sulfur.

Any mineral acid might be used for acidifying the solution preparatory to dispersion, but only sulfuric acid and sulfur dioxide gas have been employed, mainly on account of their cheapness. The former has been entirely displaced by the latter.

Solutions may be acidified by bubbling $SO_2$ through them; by passing the gas and solution countercurrent through a tower filled with packing or wooden grids; by spraying the solution into the gas through spray nozzles or other devices; or by bringing together the gas and solution in gas scrubbers.

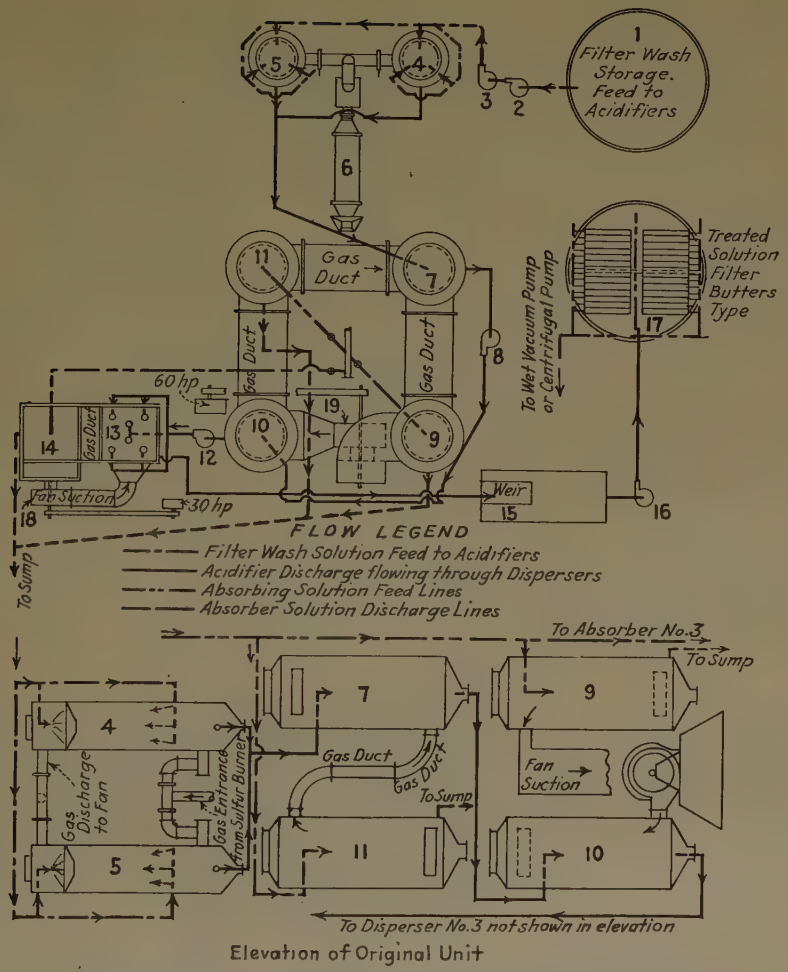


FIG. 2.—GENERAL ARRANGEMENT OF CYANIDE-RECOVERY PLANT.

1. Feed to acidifiers.
2. Acidifier feed pump, 5 hp.
3. Acidifier feed pump, 10 hp.
4. Acidifier, 6 ft. by 30 ft. 6.5 in.
5. Duplicate of 4.
6. Sulfur burner, 30 in. by 8 ft.
7. Disperser No. 1, 8 by 23 ft.
8. 5-in. centrifugal pump, 5 hp.
9. Absorber No. 1, 8 by 23 ft.
10. Disperser No. 2, 8 by 23 ft.
11. Absorber No. 2, 8 by 23 ft.
12. 5-in. centrifugal pump, 10 hp.
13. Disperser No. 3, 6 by 6 by 24 ft.
14. Absorber No. 3, 6 by 6 by 24 ft.
15. Sump for treated solution.
16. 4-in. centrifugal pump, 15 hp.
17. Treated solution filter.
18. Fan, 12,000 cu. ft. per minute.
19. Fan, 22,000 cu. ft. per minute.

Remembering the difficulty with lime in the experimental unit and anticipating similar trouble in the new plant, two steel towers 6 by 31 ft. of No. 10 gage steel were erected to act as acidifiers. Either could be "cut out" at will while the other continued to operate. These towers, like the absorbers and dispersers, have conical bottoms. From a point 4 ft. above the bottoms to 5 ft. from the top, a height of say 22 ft., wooden slats or grids, staggered, were supported at 15-in. intervals on angle iron. Their purpose was to bring about intimate gas-solution contact.

The gas from the sulfur burner enters the side near the bottom of each acidifier, while the solution entering at the top and center of each was more or less evenly distributed over the top grids by means of a launder type distributor; it trickled down over the grids and discharged at the bottom and front. From the acidifiers the acidified solution passed through a 40-in. weir, acting also as a seal, and on to the first of two dispersers, entering the top of the latter by gravity flow.

The acidifying towers were so piped up that solution and gas could pass through either tower alone, through both towers in parallel, or the solution could pass through both towers in series, whereas the gas could go through one only or through both in parallel. Later, additional gas connections were made so that the $SO_2$, as well as the solution, could pass through both towers in series, and countercurrent.

### *Liming Troubles*

Although no trouble from deposition of lime was encountered in the experimental unit at Fresnillo, this did arise in the large recovery plant, and a visit was made there to observe the process on a large scale. It appeared that it might be possible, where duplicate acid towers were available, to redissolve the deposited lime in one by circulating through it the acid solution discharge from the other. This was tried when the new plant started work at Santa Gertrudis, but a 24-hr. accumulation of lime in one acidifier could not be dissolved out by circulating through it for 24 hr. the acid solution from the other acidifier. The grids became heavily loaded with a deposit containing 39.0 per cent. CaO and 38.9 per cent. $SO_2$ and prevented the normal flow of gas and solution. Other methods were tried to keep the grids clear, but eventually they were discarded in favor of an inverted truncated cone at the top of the acidifier with a distributing overflow well suspended above it. This device had supplanted the grids at Fresnillo, but at Santa Gertrudis its efficacy was not all that was desired. Again, other devices were tried.

Meanwhile the lime precipitated out as a dense, hard, bonelike material in the circulating pump and solution pipes, and had to be dug out. Additional gas connections were made so that the $SO_2$, as well as the solution to be acidified, could be passed through both acidifiers in series, the weaker $SO_2$ coming into contact with the feed solution as the latter

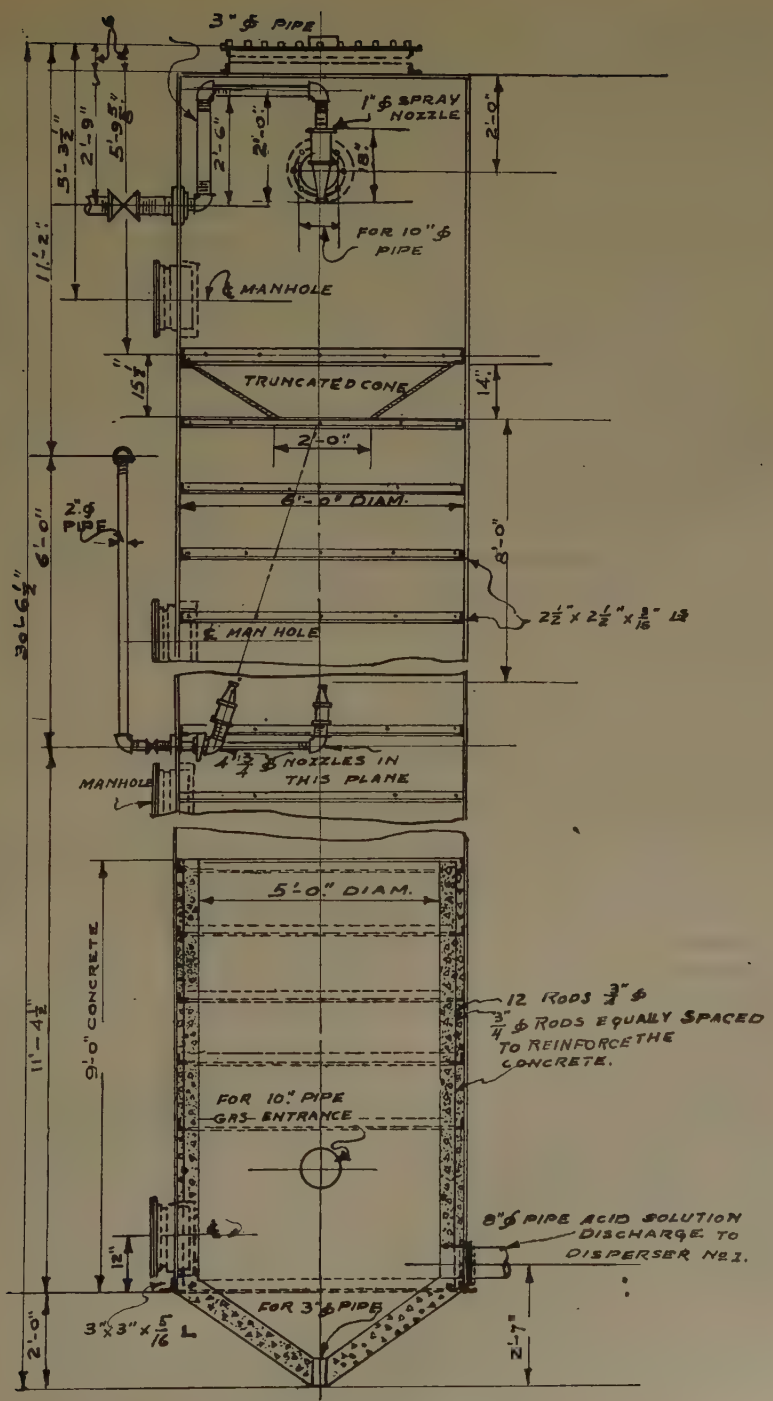


FIG. 3.—DETAILS OF ACIDIFIER.

entered the first acid tower. This arrangement resulted in reducing stack losses of sulfur and HCN, but caused deposition of lime in the circulating pump to such an extent that this arrangement had to be abandoned.

Finally, it was decided to try spray nozzles (Shutte and Koerting type) from the top and bottom of the acidifier. Briefly, four ¾-in. nozzles were arranged on the same plane near the bottom of the acidifier and impinged against a 12-in. pipe suspended from the top cone. The pressure developed by two pumps in series was 29 lb. per sq. in. at the nozzles. The use of nozzles has been entirely satisfactory; lime continues to be deposited and can not be prevented, but it is on the sides of the towers. As now operated, each acidifier is independent and is cut out and cleaned after a 15 or 20-day run. The solution pipes also require cleaning, but only once in 2 or 3 months. In acidifying 85 tons of solution per hour, the actual quantity of lime left in an acidifier in 24 hr. is 436 kg. (959 lb.) of $CaSO_3$ with 35 per cent. moisture.

Although the interior of the acidifiers was painted with hot asphalt, some pitting and scaling and eventually holes were discovered near the bottom. A 6-in. concrete lining was then put in to a height of 9 ft. and has stopped further corrosion. Fig. 3 shows details of an acidifier.

### *Sulfur Burner*

The sulfur burner used for the production of $SO_2$ is a rotary machine 30 in. dia. and 8 ft. long made by the Glen Falls Machine Works, Glen Falls, N. Y.

This machine is a revolving cylinder containing a molten bath of sulfur into which sulfur is continuously fed from a small hopper by means of a screw feeder operated by sprockets connected to the mechanism revolving the burner. The whole machine is operated by a 1-hp. motor, belt-connected to reduce the original speed.

The burner originally made 1 r.p.m. but as The Merrill Co. advised a lower speed a reduction was made to 1 r.p.3m.; later the speed was still further reduced to 1 r.p.6m.

The burner discharges its gas into a small cast-iron combustion chamber through a cylindrical connection containing four portholes with sliding dampers. This connection is bolted to the combustion chamber and in order to connect the burner to the chamber the discharge of the former carries a movable ring, called a sleeve damper, which can be opened to leave a space of 2 in. between the two, or it can be closed completely. This damper is always left slightly open for the double purpose of admitting air to the combustion chamber and permitting the accumulation of ash in the burner to discharge automatically. At our plant the ash must be raked out about once a month, when the accumulation begins to interfere with the proper operation of the burner.

During the first few months of operation the manipulation of the burner, in order to obtain proper acidulation without an undue consumption of sulfur, gave us much trouble, mainly the dampers, but probably due to our ignorance of its operation and to the fact that the feed to the acidifiers varied over a wide margin in its cyanide content. Any variation of consequence in solution-feed titrations caused a variation in the acidity of the solution being dispersed, and this change in acidity started us regulating the dampers again.

At this time Haun, at Fresnillo, suggested that sulfur consumption could possibly be reduced by covering the cylindrical portion of the burner with asbestos.

At the time the plant was laid out, the burner was placed just below and between the two acidifiers because it was thought that the burner operator should be at all times near the acidifiers; also because the nearer the burner to the acidifiers the shorter and simpler the pipe connections between the two.

After operations were begun, it appeared that it was theoretically poor practice to take excessively hot gas for absorption purposes; at least it is directly contrary to the law of the solubility of gases. For this reason it appeared that an asbestos cover would tend to make the gas leaving the burner still hotter so that the absorption of the $SO_2$ in the acidifiers would be less, consequently the stack losses would be greater. However, as it was claimed at Fresnillo that by covering the burner the sulfur consumption was reduced, this was done at Santa Gertrudis. The operation of the burner did improve and the sulfur consumption dropped somewhat. Later, the asbestos cover was left off and, probably through growing familiarity with the burner, it is working fairly well, although an improved type might be designed.

One reason for the burner troubles at first was that we were carrying a much higher acidity than necessary. It has been discovered since that the higher the acidity the more difficult it is to regulate the burner properly, and the greater the sulfur consumption, even when taking the additional acidity into consideration.

For satisfactory operation of the burner the principal requisites are (1) a constant volume of solution feed to the acidifiers containing as nearly a uniform cyanide and lime content as possible; (2) a positive and unchanging volume of air being drawn through the burner; and (3) as little manipulation of the dampers as feasible. The lower the cyanide and lime in the solution being acidified, especially the latter, the lower the acidity that can be carried and the easier the burner will be to operate and regulate.

### *Proper Acidity and Color of Solutions*

What the proper acidity of the acidifier discharge should be will be governed by the dispersion; in other words, a proper balance between

sulfur consumption and cyanide dispersed must be arrived at. As an assistance to the proper regulation of the acidity, the burner should be placed near the last disperser discharge so that the burner operator can at all times see the final spent solution and can, when necessary, test it frequently.

When the solution to be treated contains either silver or copper the last disperser discharge, if it has been sufficiently dispersed and contains enough free $SO_2$, will be milky in color. If this color disappears, as a rule, the acidity to methyl orange has been lost and the silver or copper or both are still in solution. If the burner operator is near by he will notice this at once and can then regulate the burner to bring back the acidity without loss of time.

When the flow of solution is first started through the acidifier, the solution discharging from the last disperser may be white, even when the solution is alkaline. This will be due to lime in suspension and can be easily distinguished, after a little practice, from the white color of a properly acidified solution.

### *Sulfur Consumption*

Next to the total percentage dispersion obtained, the item of sulfur consumption is the one given most attention; in fact, at the beginning of operations one is liable to place too great a stress upon the importance of saving sulfur, whose cost is the largest item (57 per cent.) in the operating expense.

The whole question of sulfur consumption is this: Will an increase in the sulfur consumed produce a sufficient increase in cyanide dispersed to show a profit over and above the cost of the extra sulfur? As mentioned elsewhere, an economic balance between the sulfur burned and the cyanide dispersed must be arrived at for any given dispersion and absorption capacity.

Whether the sulfur actually consumed is too high may be determined by comparing the quantity burned with the theoretical amount required for a solution containing the same amount of protective alkalinity as CaO, cyanide as KCN, and the acidity carried. The theoretical quantities are derived from the following equations:

$$2KCN + H_2SO_3 = K_2SO_3 + 2HCN \qquad [1]$$

or, 130.226 parts of KCN equals 32.06 parts of sulfur,
whence, 1 part of KCN equals 0.246 part of sulfur

and

$$CaO + H_2SO_3 = CaSO_3 + H_2O \qquad [2]$$

or, 56.07 parts of CaO equals 32.06 parts of sulfur,
whence, 1 part of lime (CaO) equals 0.57 part of sulfur.

The percentage of acidity is reported in terms of CaO and is the acidity to phenolphthalein. This represents either bisulfites, free $SO_2$, or

both. This acidity figure represents the amount of CaO that would be required to neutralize the acidity, and is not, therefore, the acidity itself. To convert the percentage acidity to kilos of sulfur per ton of solution the acidity is first converted into kilos of CaO per ton of solution, then multiplied by the factor 0.57, as obtained from equation 2. For example: given a solution with the following composition, 0.09475 per cent. total KCN, 0.0694 per cent. CaO as protective alkalinity, and 0.085 per cent. acidity to phenol, the theoretical amount of sulfur called for would be:

$$0.09475 \text{ per cent. KCN} = 0.9475 \text{ kg. KCN per metric ton}$$
$$0.9475 \text{ kg. KCN} \times 0.246 = 0.233 \text{ kg. of sulfur}$$

$$0.0694 \text{ per cent. CaO} = 0.694 \text{ kg. CaO per metric ton}$$
$$0.694 \text{ kg. CaO} \times 0.57 = 0.395 \text{ kg. of sulfur}$$

$$0.085 \text{ per cent. acidity} = 0.85 \text{ kg. CaO per metric ton}$$
$$0.85 \text{ kg. CaO} \times 0.57 = 0.484 \text{ kg. of sulfur}$$

$$0.233 + 0.395 + 0.484 = 1.112 \text{ total kg. of sulfur required.}$$

Therefore, 1.112 kg. of sulfur per ton of solution acidified, of the above analysis, is the theoretical amount of sulfur required to neutralize the alkalinity and to produce the acidity of 0.085 per cent. lime equivalent.

The acidity taken for the calculation must be that of the acidifier discharge, because a variable portion, depending on the initial acidity and the quantity of air circulating through the dispersers and absorbers, is driven off in the former.

With a solution of the cyanide and lime contents given, the only legitimate saving of sulfur that could be made would be that equivalent to the acidity. With a constant air and solution flow through the dispersers the acidity could be reduced and sulfur saved, but possibly only at the expense of reduced dispersion.

Taking the solution given, if the tonnage acidified and dispersed were reduced sufficiently it would be possible to decrease the acidity so that the consumption of sulfur to produce it would be almost zero, or say, 0.650 kg. total sulfur consumption in the place of 1.112 kg. On the other hand, if the tonnage of solution dispersed were not lowered, but, instead, the circulating air was greatly increased and possibly the disperser grids given a closer spacing, the same reduction in acidity could doubtless be obtained with its equivalent saving in sulfur.

The actual consumption of sulfur will, therefore, depend mostly on the lime alkalinity in the solution to be acidified and on the acidity that it will be found necessary to maintain in order to make the most economical extraction.

There is a certain loss of $SO_2$ up the stack and a further small loss as elemental sulfur that is volatilized and driven over into the acidifier from the burner. As shown in Table 1, the stack loss of sulfur is negligible, while the loss in the volatile form can not be great because the actual sulfur consumed is always close to the theoretical.

### *Stack Losses of HCN and $SO_2$*

The stack losses, which have always been with us and which we still have, are small when the plant is running normally. During temporary periods of excess acidity these losses may assume serious proportions, but as these periods usually last for minutes only, the total loss is insignificant. The stack loss of HCN is always greater than that of the sulfur. The HCN lost is determined by passing 50 l. of the stack gas through a 1 per cent. solution of caustic soda contained in four absorption bottles. The total sulfur lost up the stack is considered to be unabsorbed $SO_2$ and is determined by passing 50 l. of the stack gases through N/10 iodine and titrating the unconsumed iodine with N/10 thiosulfate.

The stack losses of sulfur are not disturbing us as much at present as formerly because it has been found that they are such a small part of the total sulfur consumed. Table 1 gives the results of a number of determinations made to indicate the losses of HCN and sulfur up the stack when operating under different conditions. As the consumption

TABLE 1.—*Determined Stack Losses of HCN and S*

| Size of Opening in Cone at Top of Acidifier, Inches | Volume of Gas, Cu. Ft. per Min. | Solution Acidified, Tons per Hour | KCN, Loss per 24 Hr., Kg. | Sulfur, Loss per 24 Hr., Kg. |
|---|---|---|---|---|
| 36 | 812 | 85 | 47 | 13 |
| 36 | 812 | 93 | 57 | 11 |
| 36 | 830 | 85 | 58 | 24 |
| 18 by 24 pipe | 549 | 64 | 33 | 9 |
| 18 by 24 pipe | 950 | 85 | 44 | 10 |
| 18 by 24 pipe | 549 | 78 | 16 | 5 |
| 18 by 16 pipe | 662 | 85 | 10 | 3 |
| 12 by 16 pipe | 662 | 85 | 7 | 3 |
| 12 by 16 pipe | 603 | 85 | 8 | 3 |

of sulfur is slightly more than 1 kg. per ton of solution acidified, 87 kg. is added to the burner hopper per hour.

### *Dispersion*

In the dispersing operation the cyanogen gas (HCN) that was formed in the acidifier, and which remains in the acid solution going to the dispersers, is removed. This gas is dissolved in the solution and although it can be removed with comparative ease, it is sufficiently fixed in the

acidified solution so that upon passage through a weir box open to the atmosphere, and 6 ft. long, no loss of HCN can be detected by means of the silver nitrate titration of the solution as it enters and leaves the weir. However, there is a slight loss as at times an odor of HCN can be easily detected.

As the cyanide in the acid solution going to the dispersers, or decyaniding tanks, is in the form of a gas dissolved in a solution, it could be removed by heating the solution to boiling, when the HCN would leave together with water vapor. If the acid solution in the dispersers were subjected to a high vacuum either at normal temperatures or upon heating, the HCN would be removed in the same way that air and dissolved oxygen are removed from a pregnant solution in Crowe vacuum tanks (Halvorsen process).

Up to the present time the only practicable means of removing the HCN from the acidified solution has been the application of vacuum, as used in the Halvorsen process, and blowing air, as applied in the Mills-Crowe system. In the latter process, which is the one used both here and at Fresnillo, a large volume of rapidly moving air is brought into contact with the acidified solution spread over a great amount of surface. This surface exposure is here obtained by filling the dispersers with wooden grid work. Bubbling air through a body of the acidified solution, as is done in laboratory testing, was tried first, but this method was not satisfactory.

Solution surface exposure may be obtained by the utilization of grids, spray nozzles, or mechanical spraying devices, but whatever method is used the aim is to obtain the most intimate contact possible between solution and gas, with the minimum resistance to air flow, smallest expenditure for power, and the least outlay for upkeep.

With our high-lime solutions a considerable amount of a hard bone-like deposit of calcium sulfite precipitates out on the grids, especially in the first disperser; a certain amount of muck also collects in the side launders of the solution distributor used to spread the solution more or less evenly over the top grid set. For these reasons, even were it known that spray nozzles similar to those in the acidifiers would break up the solution to a greater extent than grids, it is doubtful if they would be used. The possibility of obstructions putting all or part of them out of commission would be too great. Besides, the plant site permits of running the acidifier discharge to No. 1 disperser by gravity, which not only saves from 10 to 15 hp. daily, but obviates daily shutdowns due to liming up of any pump that might be used to spray the acid solution into the disperser.

*Distribution of Solution*

In all cases where grids or similar types of tank filling are used, the first essential is that the solution entering should be as evenly and

uniformly distributed over the top grids as possible. As the main object is to obtain the maximum amount of solution surface exposed to the air with a minimum of tank resistance, this result can not be obtained with certainty unless all of the top grids receive their proportion of the feed.

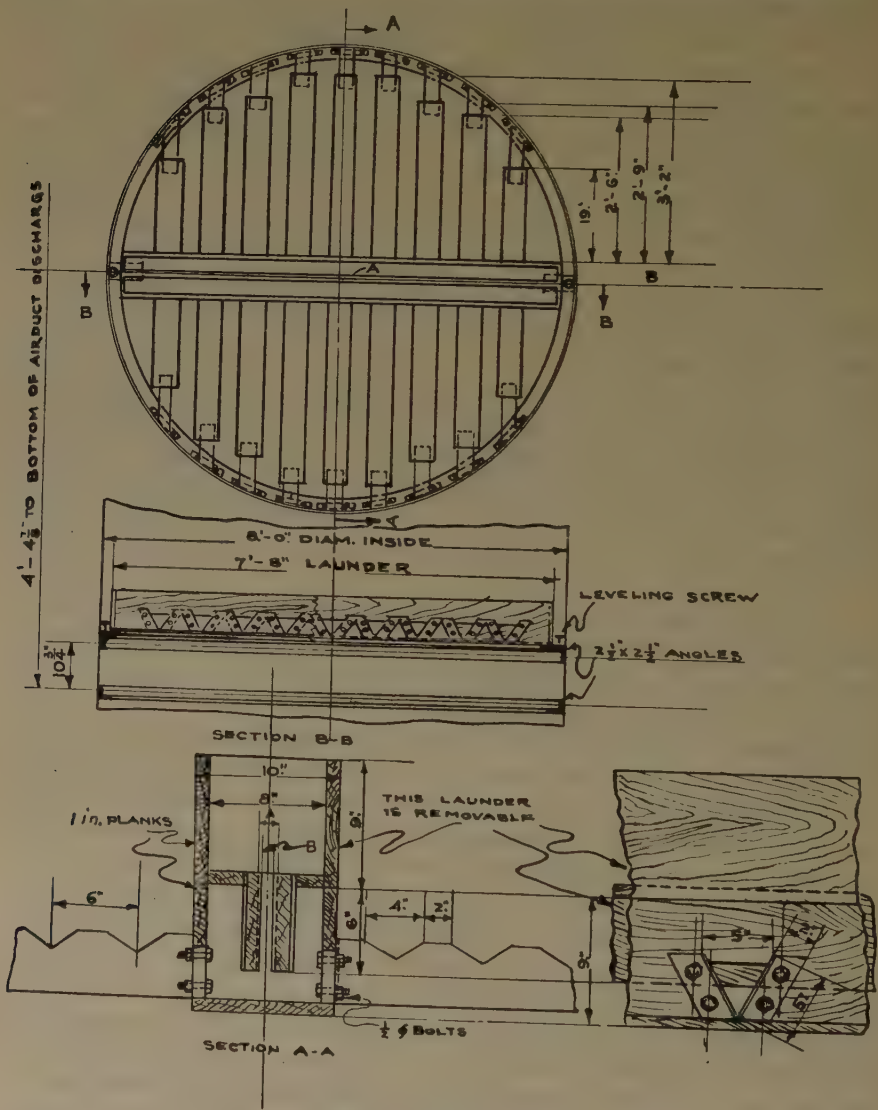


FIG. 4.—DETAILS OF DISTRIBUTING LAUNDERS FOR DISPERSERS 1 AND 2.

Where there is a considerable distance between the distributor and the top grid set, or between the individual sets, it is more than likely that the air rushing through will swirl the falling solution about and

thus make up for the inefficiency of the distributor itself. However this may be, with excellent solution distribution at the top, poor work that may develop can not be blamed on the distribution.

Fig. 4 shows the design of the distributors as used in our dispersers and absorbers, except in absorber No. 3. As can be seen, the distributor is composed of a central launder of wood to which are bolted on both sides equally spaced V-shaped launders of $\frac{1}{16}$-in. sheet steel. The side launders have notches cut in their upper edges through which the solution overflows. The solution enters through the side of the disperser and discharges from above into the central portion of the center launder, then flows out through and overflows from the side launders.

Considerable difficulty was encountered when the plant first started, in getting the solution to flow uniformly from the central launder into all the side launders. On account of feeding the solution into the middle of the central launder, most of it ran to the ends and then out those side launders, leaving the central portion of the tank with very little distribution. Baffling in the central launder was tried but was unsatisfactory. Finally an auxiliary launder was set on top of the central one. It has a slot in its bottom for the full length and extended to within an inch or two of the bottom of the lower central launder. This has given complete satisfaction.

The 8-in. pipe that carries the solution from the acidifier weir to No. 1 disperser has been cleaned once since the plant started. The distributor launders are cleaned during the regular monthly shutdown.

### *Air-solution Contact*

Dispersion is increased with an increase in the solution surface exposed to a given volume of air, therefore care must be exercised to obtain the best air-solution contact. At Santa Gertrudis, circular angle iron was riveted to the inside shell of the tank at 15-in. intervals. On these were laid wooden grids, 16 sets of 1 by 6-in. pieces 2 in. apart in disperser No. 1 and 24 sets of 1 by 4-in. pieces 1-½ in. apart in disperser No. 2. They were nailed together in groups to facilitate installation and removal for cleaning, and their sides were parallel to the flow of air. Liming of the grids has given more or less trouble and they have to be cleaned when the lime on them increases the resistance to the air flow. In this plant the dispersers and absorbers are in closed circuit. The latter have nine sets of grids. With the present installation, when the fan is in good order, the best volume of air obtainable is 23,000 cu. ft. per min. against a static pressure of 4.8 in. of water.

The rate of dispersion increases with an increase in acidity and temperature of the solution being dispersed, up to an optimum, of course, where the air volume is constant. It was found during a period of cold

nights (40° to 45° F.) that dispersion was lower than during the day, when it was warmer. But as heating was impracticable it was not attempted. As higher temperatures give better dispersion but cause an increase in deposition of lime, a study was made of the possibilities of neutralization of the acidifier feed and removal of precipitated calcium sulfite before dispersion. The conclusions arrived at are as follows:

From a construction viewpoint, a preliminary neutralization of the solution to be dispersed would necessitate a more expensive installation (two neutralizers and one acidifier in place of two acidifiers as at present; one, and possibly two, covered Dorr thickeners with Dorrco pumps; one small Hardinge roller spray absorber with fan; and one small Roots blower). From an operating standpoint the removal of the lime as $CaSO_3$ before acidification should increase dispersion and would allow of a more complete precipitation of the copper and silver, where present; it would permit of heating the solution where this was found advisable; and it would eliminate all labor now required to remove lime deposits from the acidifiers, pipe lines, and disperser grids, besides making a possible saving in sulfur consumption.

### *Air Required for Dispersion*

The amount of air available depends primarily on the type and size of fan or blower used. However, the actual amount of air flowing, as determined by Pitot-tube readings, will depend on the condition (lime accumulation) of the fan or blower; the speed at which it may be safely and economically operated to produce the greatest volume; and the resistance of the towers and air ducts of the system. This resistance in turn varies with the type, number, arrangement and spacing of the grids; amount of solution dispersed, tonnage of absorbing solution and size and form of the connecting air ducts.

As the fan suction is connected to the top of an absorber, a certain amount of absorbing solution is constantly being carried over as spray into the fan, where it gradually builds up a deposit of lime ($CaCO_3$) upon the blades. The greater this deposit, the less air is delivered, beside the danger of unbalancing and wrecking the fan, especially when the latter is running at its maximum speed.

Experimental work done at Fresnillo indicated that 15 cu. ft. of air per min. per ton of solution treated per 24 hr. would give the maximum economical extraction on the solutions worked with there. Although this figure may be decreased with a decrease in the lime and cyanide contents of the solution to be treated, also with an increase in the acidity up to a certain point, yet it would appear from our work at Santa Gertrudis that this quantity should be taken as a minimum rather than as a maximum for the amount of air to give the best dispersion results.

Although to some extent an increase in acidity will accomplish the same result as more air, we have found that the plant as a whole operates more smoothly and gives a higher extraction when using the maximum amount of air obtainable. Under such conditions a low acidity to phenolphthalein can be carried and yet have the last disperser discharge acid to methyl orange. The relation between air and acidity of the solution being dispersed is an important one and will depend entirely on the former because that will usually be a more or less fixed quantity. Table 2 gives an idea of the effects of acidity on dispersion. The acidity given is that determined by titrating with caustic, using phenolphthalein as an indicator, and represents the total acidity due to the bisulfites, plus that of the free $SO_2$. This acidity, while important, is not so much so as the acidity to methyl orange, the latter representing the acidity due to free $SO_2$ only. In order to get the greatest amount of dispersion it is necessary that the last disperser discharge should contain free $SO_2$, especially where the solution contains silver and copper. Table 3 illustrates the importance of free $SO_2$ in the final disperser discharge.

TABLE 2.—*Effect of Acidity on Dispersion*

| Solution Acidified, Tons per Hour | Acidifier Feed | | Disperser No. 1 Tails | | Disperser No. 2 Tails | | Disperser No. 3 Tails | | |
|---|---|---|---|---|---|---|---|---|---|
| | KCN, Per Cent. | CaO, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | Acidity, Per Cent. |
| 83.9 | 0.100 | 0.070 | 0.0600 | 40.0 | 0.0190 | 81.0 | 0.008 | 92.0 | 0.052 |
| 83.9 | 0.100 | 0.067 | 0.0500 | 50.0 | 0.0140 | 86.0 | 0.005 | 95.0 | 0.084 |
| 83.9 | 0.095 | 0.070 | 0.0500 | 47.3 | 0.0160 | 83.1 | 0.007 | 92.6 | 0.057 |
| 83.9 | 0.093 | 0.067 | 0.0500 | 47.3 | 0.0150 | 84.2 | 0.006 | 93.6 | 0.065 |
| 83.9 | 0.100 | 0.073 | 0.0500 | 50.0 | 0.0155 | 84.5 | 0.007 | 93.0 | 0.062 |
| 83.9 | 0.100 | 0.073 | 0.0500 | 50.0 | 0.0135 | 86.5 | 0.0055 | 94.5 | 0.074 |
| 86.9 | 0.095 | 0.064 | 0.0525 | 44.7 | 0.0210 | 77.8 | 0.008 | 91.5 | 0.047 |
| 86.9 | 0.095 | 0.062 | 0.0500 | 47.3 | 0.0145 | 84.7 | 0.005 | 94.7 | 0.060 |
| 86.9 | 0.100 | 0.070 | 0.0575 | 42.5 | 0.0225 | 77.5 | 0.009 | 91.0 | 0.063 |
| 86.9 | 0.100 | 0.073 | 0.0550 | 45.0 | 0.0170 | 83.0 | 0.007 | 93.0 | 0.068 |
| 86.9 | 0.100 | 0.073 | 0.0500 | 50.0 | 0.0155 | 84.5 | 0.006 | 94.0 | 0.074 |

* Unless otherwise stated, the CaO in the acidifier feed is the lime alkalinity to phenolphthalein; whereas the acidity is the titration with caustic using phenolphthalein indicator. This acidity is reported in terms of CaO; that is, the CaO as reported is the amount that would be required to neutralize the acidity.

It will be observed that in all cases the total dispersion increases with an increase in the total acidity of the discharge from No. 3 disperser. Although as a generality it may be said that an increase in the total acidity will increase the total dispersion, nevertheless it has been noted many times that where the total acidity is high the methyl-orange

titration may be low, and the dispersion also low. From this we have come to the conclusion that the total acidity is of less importance than the methyl-orange acidity, or the presence of free $SO_2$ in preference to bisulfites. If this is so, the total acidity may be very low and still a good dispersion may be obtained, provided that the methyl-orange acidity is sufficiently high. In support of this assumption Table 3 is given.

Although this table appears to prove that the total dispersion increases with an increase in the methyl-orange acidity, there are enough exceptions so that the proof is not absolute. However, the differences in the methyl-orange acidities that cause the exceptions are so small that they might easily be due to errors in titrations.

Although a good dispersion can be obtained with a low total acidity and a high methyl-orange acidity, this condition can not be obtained in the presence of high lime, except by means of increased air per given volume of solution passing through the dispersers. Air, therefore, and plenty of it, seems to be the whole question of dispersion (bisulfites plus air = normal sulfites plus $SO_2$).

The following average figures, the result of hourly samples taken during an ordinary day shift of 9 hr., show how much $SO_2$ is driven off in the dispersers and absorbed in the absorbers; they also indicate the saving in sulfur that is possible with sufficient increase in air: Average acidity of the acidifier discharge, 0.085 per cent.; disperser No. 1 discharge, 0.074 per cent., disperser No. 2 discharge, 0.067 per cent., and disperser No. 3 discharge, 0.059 per cent., a total loss of acidity in the dispersers of 0.026 per cent. This is equivalent to 0.26 kg. of CaO, or 0.148 kg. of sulfur per ton of solution dispersed. In other words, not only were 148 g. of sulfur lost for each ton of solution dispersed, but there were also consumed 260 g. of CaO per ton of solution dispersed by the absorbing solution in neutralizing this lost sulfur.

Under normal operating conditions, the discharge from the acidifier never contains free $SO_2$, the acidity to phenolphthalein must, therefore, be due to bisulfites alone. (Normal sulfites have no acid reaction.)

When air is passed through a solution of bisulfites the latter are broken down into normal sulfites with the liberation of free $SO_2$. This being so, it is evident that if sufficient air were available it would be possible to take an acidifier discharge titrating, say, 0.085 per cent. acidity to phenolphthalein (bisulfite acidity), with no acidity to methyl orange (free $SO_2$), and convert the total acidity completely into acidity due to free $SO_2$, through the breaking-down process. If this were done, however, the greater part of the liberated $SO_2$ would be driven over into the absorbers along with HCN, thus destroying excessive quantities of lime in the absorbing solution.

As the average acidity of the acidifier discharge is 0.085 per cent. to phenolphthalein and the No. 3 disperser discharge is 0.059 per cent., a

TABLE 3.—*Effect of Free $SO_2$ in the Final Disperser Discharge*

| Solution Acidified, Tons per Hour | Acidifier Feed | | Disperser No. 1 Tails | | Disperser No. 2 Tails | | Disperser No. 3 Tails | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Acidities, Per Cent. | |
| | KCN, Per Cent. | CaO, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | KCN, Per Cent. | Dispersion, Per Cent. | Phenolphthalein | Methyl Orange |
| 83.0 | 0.090 | 0.081 | 0.050 | 44.4 | 0.020 | 77.7 | 0.008 | 91.1 | 0.053 | 0.008 |
| 83.9 | 0.090 | 0.084 | 0.045 | 50.0 | 0.015 | 83.3 | 0.006 | 93.3 | 0.061 | 0.014 |
| 83.9 | 0.095 | 0.084 | 0.050 | 47.3 | 0.020 | 78.9 | 0.009 | 90.5 | 0.055 | 0.008 |
| 84.9 | 0.095 | 0.081 | 0.0475 | 50.0 | 0.0115 | 87.8 | 0.0055 | 94.2 | 0.070 | 0.016 |
| 84.9 | 0.085 | 0.087 | 0.0475 | 44.1 | 0.015 | 82.3 | 0.0065 | 92.3 | 0.067 | 0.014 |
| 84.9 | 0.085 | 0.084 | 0.0375 | 55.8 | 0.011 | 87.0 | 0.0045 | 94.7 | 0.069 | 0.018 |
| 78.8 | 0.095 | 0.084 | 0.0475 | 50.0 | 0.012 | 87.3 | 0.005 | 94.7 | 0.075 | 0.014 |
| 78.8 | 0.095 | 0.084 | 0.0500 | 47.3 | 0.013 | 86.3 | 0.006 | 93.6 | 0.050 | 0.010 |
| 79.5 | 0.110 | 0.084 | 0.0625 | 43.1 | 0.0215 | 80.4 | 0.009 | 91.8 | 0.076 | 0.014 |
| 79.5 | 0.110 | 0.087 | 0.0525 | 52.2 | 0.0145 | 86.8 | 0.0055 | 95.0 | 0.089 | 0.018 |

considerable saving in sulfur could be made if the air volume passing through the dispersers could be increased sufficiently to permit a reduction in the acidity of the acidifier discharge from 0.085 to 0.059 per cent. or even less.

Although it is not actually true, the experience so far gained during the past year of operation of the recovery plant would indicate that if enough air were available, this additional air in combination with a sufficient number of grids properly arranged would enable us to maintain the present extraction when treating 1900 to 2000 tons of solution per

TABLE 4.—*Strength of Solutions at Various Points*

| | |
|---|---|
| Acidifier feed: | |
| KCN, per cent | 0.09475 |
| CaO as protective alkalinity, per cent | 0.0694 |
| Acidifier discharge: | |
| Acidity to phenol., per cent | 0.085 |
| No. 1 disperser tails: | |
| Acidity to phenol., per cent | 0.0743 |
| KCN, per cent | 0.051 |
| No. 2 disperser tails: | |
| Acidity to phenol., per cent | 0.067 |
| KCN, per cent | 0.0149 |
| No. 3 disperser tails: | |
| Acidity to phenol., per cent | 0.059 |
| KCN, per cent | 0.0063 |
| Acidity to methyl orange, per cent | 0.016 |

day, with an acidifier discharge running from 0.03 to 0.04 per cent. total acidity (phenolphthalein titration). Although such a low acidity would not produce any saving in absorbing solution lime, especially if it were all

converted to free $SO_2$, nevertheless the saving in sulfur would be from 256 to 313 g. per ton of solution acidified; or 512 to 626 kg. per day based upon 2000 tons of solution treated per 24 hours.

The average of 10 titrations to show the strength of the solutions at different points in the plant, with particular reference to lime and acidity, are given in Table 4.

### *Absorption*

Absorption may be carried out economically in two ways, either by passing the absorbing solution and gas to be absorbed countercurrent through a tower containing checkerwork, grids, or other material offering great surface area and a multitude of voids; or by breaking up the absorbing solution in the presence of the gas to be absorbed by means of spray nozzles in vertical towers, or by means of mechanical sprayers such as revolving cylinders, brushes, or disks in horizontal spray chambers. The latter may be constructed exactly like the vertical tower but placed horizontally. Our absorbers are 8 ft. dia. and 21 ft. high. Each contains nine sets of 4-in. grids placed vertically with the slats spaced 1½ inches.

Both methods have their good and bad points. Which system should be used will depend to a great extent on the conditions encountered in the individual cyanide plant and the cost of power. Where a large volume of absorbing solution is available for passage by gravity through a vertical tower, grids would appear to be the logical choice; with the possible addition of one or two small fine sprays in the air ducts leading from the dispersers to the absorbers. These sprays would not only greatly increase the absorption but they would also protect the steel duct, if steel were used, from the corrosive effects of the acid spray which is always carried over in varying quantities from the dispersers to the absorbers.

Proper distribution of the solution over the absorbers is as important as in the dispersers already described.

Tower packing, of the type commonly used in the different chemical industries in absorption apparatus, could not be used to advantage, according to our experience, because of the excessive resistance to the air flow and to the gradual liming-up of the packing, especially in the lower section.

Where a large gravity flow of absorbing solution (4.5 to 5.0 tons or more per ton of solution dispersed) is at hand entailing no extra pumping, wooden grids or checkerwork should be used. These grids have to be removed from the tank every two or three months for cleaning; the frequency of this depends on the cleanness of the absorbing solution and the acidity of the solution being dispersed. The grids, therefore, should be built and installed in such a way as to be placed easily and quickly in the absorber or removed therefrom.

The spaces between the grids should be as small and the grids as close together as possible, commensurate with the volume of air and solution available, and the freedom of the latter from chips, sticks, slime, etc. Our grid spacing—that is, the spaces between the individual slats making up the grid sets—is 1½ in. in all towers, but closer spacing would improve both dispersion and absorption, provided that a greater volume of air could be obtained, or rather provided that the same volume of air as at present could be maintained with the closer grid spacing.

Where the tonnage of absorbing solution is small, or where conditions are such that it would be necessary to pump all of the absorbing solution required, the best form of absorption apparatus would probably be the horizontal spray chamber containing revolving cylinders or brushes operating at 900 to 1000 r.p.m. In this type of machine the absorbing solution enters one end, is picked up and sprayed again and again by the high-speed cylinders, and then leaves at the opposite end.

The advantages of such an absorber would be the intimate contact between absorbing solution and gas; small resistance to gas flow; a minimum amount of absorbing solution required, and freedom from trouble caused from lime deposits. Although lime would be formed there would be no grids to take out, clean and replace and as the absorber is nothing more than a long wooden box with plenty of manholes, the cleaning operation would be simple.

Notwithstanding the fact that such an absorber would require the minimum amount of absorbing solution, sufficient alkali in the form of lime would have to be present to fix the dispersed HCN and to neutralize the excess $SO_2$ driven over from the disperser. Also, enough excess alkali should be present so that there would be no tendency for the cyanide in the absorbing solution itself to disperse. If the amount of lime for this purpose could not be increased by augmenting the absorbing solution flow, milk-of-lime would have to be added to the absorber solution feed.

Spray nozzles could be used in the absorbers when it is necessary to pump all of the absorbing solution; but nozzles are likely to be plugged with debris; the spray might not be fine enough; and they require more power than cylinders.

### *Completeness of Absorption*

As to the completeness of absorption, the average in absorber No. 1 is 66 per cent. and in No. 2, it is 73 per cent.

As the absorbers, dispersers and fan are in closed circuit one might think that the absorption, whether good or bad, would make little difference because all of the HCN dispersed would have to travel around the circuit until it was absorbed. However, the completeness of the absorption and the constant load of HCN in the air being circulated has a big

influence on the completeness of dispersion, inasmuch as the dispersion falls off badly whenever absorption is poor. Laboratory tests also confirmed this. Dispersion and absorption are so interrelated that it is difficult to discuss one without the other.

*Utilization of Treated Solution, Recovery of Silver and Copper*

If a filter-wash effluent is to be treated in the recovery plant this solution will always contain a varying amount of silver—in the case of silver ores—that will be thrown out as a white slimy precipitate of AgCNS in the presence of soluble sulfocyanates. (Although this precipitate mixed with CuCNS, in our case, appears slimy upon first formation, after 4 to 6 hr. standing it assumes a granular character but still continues to settle very slowly. However, it will settle in 24 hr., producing a clear supernatant solution.)

Where the silver in the wash-water effluent is considerable and the tonnage of solution treated is large, it may be found more economical or more advantageous to recover the precipitated values by filtration rather than by settlement; that is, of course, if the amount of silver and copper or either warrants the cost of such an installation.

Copper will also precipitate out as a sulfocyanate provided there are enough soluble sulfocyanates in the solution treated to combine with both the silver and copper; otherwise the latter would, no doubt, precipitate as $Cu_2(CN)_2$.

At Santa Gertrudis, so far the precipitation of the gold has been negligible, varying from zero to 1.2 parts per 10,000 parts of silver according to precipitate assays. When assaying large volumes of solutions by the evaporation method the recovery-plant treatment appears to precipitate no gold whatever. Even excessive dispersion in the laboratory on the acidifier discharge failed to show any precipitation of the gold.

Where a barren plant solution is treated, as at Fresnillo, of course no silver recovery would have to be arranged for. However, in some cases where the mill solutions are exceptionally high in copper it may be considered advisable either to settle or filter the treated solution in order to remove that element as much as possible from the circuit.

If the solution to be treated carries enough copper to remove, the problem of handling the precipitate is a troublesome one, which, fortunately, we have not had to tackle. Nevertheless, the combined precipitates of silver and copper that are continually being returned to the milling circuit are gradually building up the copper content of the mill solution to the point where it will be necessary to consider shipment of the more or less dried precipitate to the smelter; at least for a time or until the mill solutions have been cleaned up. (Note: All such precipitate is now being removed by settlement and filtration, air-dried in patios, sealed in cyanide drums, and shipped to the smelter.)

### *Filtration*

As two Dorr thickeners were available, one was used for storage of solution feed for the acidifiers and the other was converted into a Butters filter for removing the precipitated silver from the spent acid solution from the last disperser. There are two compartments, each of which holds 33 leaves 5½ by 11 ft., with vacuum connections on both sides.

Although no daily records have been kept, occasional calculations have shown that about 4¼ tons of dry precipitate is removed monthly by filtration, and for each ton of dry material so filtered there is approximately 1½ tons (dry weight) settled out in the filter tank. The latter was pumped into the slime circuit at infrequent intervals, about once every 60 days. One analysis of this settled product gave a trace of gold, 11,325 g. of silver per ton (365 oz.), 50 per cent. insoluble, 13.8 per cent. copper, and 56 per cent. moisture. The moisture is fairly constant but the copper, silver and insoluble vary.

### *Precipitation of Silver, Copper and Gold*

The precipitation of the silver and copper may or may not be complete, depending on the volume of air coming into contact with a given volume of the properly acidified solution and the presence of sufficient free $SO_2$. For some time it was thought that the complete precipitation of these metals required a fairly thorough elimination of the cyanide as well; but this is not so. Laboratory tests indicate that the greatest factors necessary for silver and copper precipitation are a large volume of air per ton of solution (15 to 20 cu. ft. per ton per 24 hr.) and the presence of the necessary amount of $SO_2$.

While operating with only two dispersers and two absorbers the silver precipitation was never complete, but since installing a third disperser with its own fan, we no longer have any difficulty in that respect. The silver precipitation is complete, but only about 90 per cent. of the copper is obtained. The complete precipitation of copper as the sulfocyanate appears to require a longer contact with air than does silver.

The gold, so far, has not been precipitated with the silver and copper, or if so, in such small amounts only that at times solution assays are shown indicating a limited precipitation and at other times no precipitation whatever.

Where the gold is high enough it might pay to precipitate both gold and silver with zinc dust, treat the barren solution in the recovery plant, and waste the spent acid solution, when mill water is plentiful. The problem of recovering silver, copper and gold in the solution to be treated is one that will vary with conditions and must, therefore, be worked out for each individual mill.

### *Spent Acid Solution as a Filter Wash*

Returning to the subject of utilization of treated solution, at most plants it will doubtless be found necessary to use the spent acid solution as a final water wash on the filters because of shortage in mill-water supply.

With most types of filters, especially the Butters and Moore, there should be no difficulty, provided that the acid solution contains no silver precipitate and very little precipitated copper. Any silver present would, of course, be lost; whereas the presence of much precipitated copper might seriously cut down the leaching rate during the water-wash period. The suggested difficulty that might arise with some classes of filters seems to apply principally to the self-sluicing type in which the filter cake is discharged by small streams of wash water issuing at high velocity from nozzles. Even with this type a means of using the recovery-plant spent acid solution after clarification could be developed provided that certain conditions were observed.

## Fans and Pumps

Fig. 2 and the general description of the recovery plant show that several fans and pumps are required, therefore a few details will be given:

*Acidifier Exhaust Fan.*—This fan is used to draw $SO_2$ through the acidifiers. It is a No. 4 Sturtevant "Monogram," belt-driven at 1448 r.p.m. by a 2-hp. General Electric motor. It draws 500 cu. ft. of gas per min., but the volume depends on the liming up of the acidifier, the quantity of ash carried over from the sulfur burner and deposited in the gas main, and the quantity of solution being acidified; the last factor has the least effect on the fan. No appreciable difference in sulfur consumption has been observed whether the volume of gas through the acidifier is 500 or 1000 cu. ft. per min. The suction in clean acidifiers ranges from 1.50 in. of water at the bottom to 2.75 in. at the top, and in a limed-up acidifier, 0.90 in. at the bottom to 2.90 in. at the top. Between the two acidifiers are permanent manometers from which may be read the resistance of the towers at top and bottom.

As to corrosion of the fan, at Fresnillo they had a cast-iron casing and sheet-iron impeller. The wet gas destroyed the latter in 36 hr., so at Santa Gertrudis the casing was made of cast bronze and the impeller of sheet copper. The first impeller ran 204 days, and after 125 days the second impeller was redipped in hot asphalt and put aside until the other one is worn out.

*Disperser and Absorber Fans.*—These units consist of one No. 9 Sturtevant "multivane" fan driven at 830 r.p.m. by a 64-hp. motor and producing 19,000 to 23,000 cu. ft. of air per min.; and one No. 4½ Sirocco fan driven at 1080 r.p.m. by a 30-hp. motor and delivering 10,000 to 12,000 cu. ft. per min. Each of these fans serves a unit. The

No. 9 fan serves two dispersers and two absorbers, whereas the No. 4½ fan is connected to one disperser and one absorber.

*Pumps.*—The function and capacity of the pumps handling 2000 tons of solution a day may be tabulated as shown in Table 5.

TABLE 5.—*Function and Capacity of Pumps*

| Function | Type and Capacity |
|---|---|
| 1. Lift (12 ft.) from storage tank and forcing through nozzles in acidifiers. | Two 5-in. Goulds closed-runner centrifugals in series, driven by 5 and 10-hp. motors. |
| 2. Lift (18 ft.) from bottom of disperser No. 1 to top of disperser No. 2. | One 5-in. Goulds centrifugal driven by 5-hp. motor. |
| 3. Lift (9 ft.) to bottom of disperser No. 3 forcing through nozzles. | One 5-in. Goulds centrifugal driven at 1750 r.p.m. by 10-hp. motor, developing 16 lb. per sq. in. at nozzles. |
| 4. Lift (55 ft.) from treated solution sump to clarifier. | One 4-in. Goulds centrifugal driven by 15-hp. motor. |

## CONTROL AND TESTING

As may be realized, careful control of this process and proper measuring, sampling, and rapid testing are essential. This is done hourly.

1. Solutions were analyzed for total constituents and for KCN content by the regular methods.

2. The solution discharge from the last disperser may be white, even when it is alkaline, when the flow is started through the acidifier. Lime in suspension causes this whiteness but it can be easily distinguished from the milkiness of a properly acidified solution.

3. Sulfur lost is determined by passing 50 l. of the stack gases through N/10 iodine and titrating the unconsumed iodine with N/10 thiosulfate.

4. Hydrocyanic gas lost is determined by passing 50 l. of stack gas through a 1 per cent. solution of NaOH contained in four absorption bottles.

5. Hourly samples of the last disperser discharge are titrated for total acidity with phenolphthalein and qualitatively with methyl orange for free $SO_2$.

6. The acidity of the disperser solutions is determined by titrating with NaOH, using phenolphthalein as an indicator. This represents the total acidity due to bisulfites, plus that of free $SO_2$. This acidity, although important, is not so much so as the acidity to methyl orange, which represents the acidity due to free $SO_2$ only.

7. In order to get some idea of the comparative efficiency of the absorbers, the tops of both dispersers and absorbers were connected by ½-in. piping which was extended into the titrating room where, by means of a connection with a wet vacuum pump, samples of gas could be drawn from the top of any tank desired. With this arrangement it was hoped

that if gas could be drawn from the top of each tank in turn for the same period, and completely absorbed in NaOH, the amounts so absorbed could be compared, thus indicating the comparative richness of the gas circulating and the amount of absorption.

8. In making laboratory dispersion tests to determine the effect of poor absorption upon the rate of dispersion the procedure is as follows: Two liters of the acidifier discharge were placed in a 2½-l. acid bottle and in one case gas from the top of No. 2 absorber, and in the other pure air was drawn through for 1 hr. by means of a connection to the clarifier wet vacuum pump. At the end of 5-min. intervals 50 c.c. was removed and placed in an Erlenmeyer flask containing quicklime, while 10 c.c. additional was taken for an acidity determination with standard NaOH. The sample containing lime was well shaken, filtered and titrated for total KCN with standard $AgNO_3$, using KI indicator. At the end of 1 hr. the final tail solution was titrated for total KCN both before and after filtering off the precipitated AgCNS and CuCNS, 50 c.c. in each case being used for these determinations. The titration after filtration was much higher than before filtration. The low titration obtained on the solution before filtering off the sulfocyanates of copper and silver is due to the fact that these precipitates slowly redissolve when the solution containing them is made alkaline. Upon going into solution, cyanide is taken up and becomes untitratable by the Liebig method.

9. As the acidifier solution feed was very low in gold content, assays were made in the usual manner by evaporating 15 l. of the solution tested.

10. When treating any working solution, be it filter-wash effluent or barren, the actual amount of cyanide possible to recover, as a rule, will be greater than that shown by the titration for total KCN. Where this occurs the difference is caused by the presence of silver and (or) copper tying up cyanide that becomes untitratable by the method used.

As the solution being treated at Santa Gertrudis contains both metals, there may be a considerable difference between the amount of cyanide recoverable and the quantity indicated as present by the acidifier feed titration, depending on the amounts of silver and copper in the feed. For example: the cyanide titrations (0.00062 per cent.) of the disperser tails after 80 min. dispersion is a great deal less than that (0.0035 per cent.) for the 2-hr. dispersion tails. The same amount of air and the same volumes of solutions were used in both groups of tests. The differences in the results are due to the fact that in the former all titrations but the last were made on solutions in which the copper and silver sulfocyanates were caused to redissolve by means of the addition of lime. While the titration for total KCN must be made in the presence of the redissolved copper and silver, in order to calculate the correct extraction on the acidifier feed, the precipitated sulfocyanates of these metals must be filtered off and the filtrate made alkaline before the total available

cyanide remaining in the disperser tails can be determined by the Liebig titration.

An idea of the actual amount of cyanide in the acidifier feed compared to the quantity shown by the titration for total KCN is obtained by stating that the average of 12 laboratory dispersion tests was 0.09092 per cent. KCN and 0.10588 per cent., respectively. (By actual cyanide is meant the total cyanide available for recovery in the recovery plant.) These tests were made in September, 1925, so they should show a smaller difference between actual cyanide and titratable cyanide than similar tests made a year later, due to the constant building up of the copper in the cyanide-plant circuit. In an effort to prove this assumption, tests made in July, 1926, gave 0.09810 per cent. KCN in the acidifier feed and 0.1166 per cent. total available KCN after absorption.

The tests for these results were made by taking 500 c.c. of the feed to the acidifier, adding a little $Na_2SO_3$ and KCNS, making acid with 30 to 40 c.c. of normal $H_2SO_4$, and dispersing for 1 hr. The HCN driven off was absorbed in a 1 per cent. solution of KOH, of which 200 c.c. was in each of four absorption bottles.

It has been found that the reason why the daily average KCN in the last disperser discharge, as indicated by the hourly titrations, is always higher than the composite sample of the same solutions for 12 hr., is that the sulfocyanates of copper and silver in the samples tested hourly did not have time to dissolve completely upon being made alkaline with lime. This gave high titrations. On the other hand, the hourly samples taken remained in contact with lime for 12 to 24 hr. before being titrated, so that the sulfocyanates had time to take up their full quota of cyanide, with resultant lower titrations.

## Costs and Profits

After our difficulties it is highly satisfying to be able to report a metallurgical and financial success. The preliminary estimate of cost was based on treating 2000 tons of solution a day containing 0.103 per cent. total KCN and 0.0726 per cent. CaO. The prices for chemicals f.o.b. plant were ₱ 100 ($50) per ton for sulfur, ₱ 40 ($20) per ton for lime (based on 100 per cent. CaO), and 50 cvs. per kg. (11.4 c. per lb.) for cyanide. Power cost 25 cvs. (12 c.) per horsepower day.

It was calculated that, with 25 per cent. additional as a factor of safety, 0.834 kg. (1.8 lb.) of sulfur would be required to neutralize the alkalinity of the KCN and lime per ton of solution acidified. If the 25 per cent. extra sulfur should be driven off in the dispersers and absorbed in the absorbers, the equivalent amount of lime destroyed would be 0.292 kg. (0.64 lb.) of CaO per ton of solution dispersed.

It was assumed that 90 per cent. of the total KCN in the solution fed to the recovery plant would be saved, or 0.927 kg. (2.04 lb.) per ton

of solution treated, and this amount of KCN would destroy 0.389 kg. (0.85 lb.) of CaO in the absorbers.

The total chemical consumption would be 0.834 kg. (1.8 lb.) of sulfur (burned) and 0.681 kg. (0.292 + 0.389) (1.44 lb.) of CaO (destroyed in absorbers) per ton of solution acidified. The estimated total cost and actual cost as of a recent month were as given in Table 6.

TABLE 6.—*Estimated and Actual Costs of Cyanide Recovery per Ton of Solution Treated*

| Item | Estimate | | Actual | |
|---|---|---|---|---|
| | Centavos | Cents* | Centavos | Cents* |
| Sulfur | 8.34 | 4.17 | 9.53 | 4.77 |
| Lime | 2.72 | 1.36 | Not charged | |
| Power | 1.00 | 0.50 | 2.73 | 1.36 |
| Labor and maintenance (1 man each shift and 1 boy on day shift) | 2.50 | 1.25 | 2.56 | 1.28 |
| Supplies | Not determined | | 1.07 | 0.53 |
| Shops | Not determined | | 0.76 | 0.38 |
| Total | 14.56 | 7.28 | 16.65 | 8.32 |

* Conversion from Mexican to American currency: 1 peso = approximately 50 cents.

Two unforeseen expenses increased the costs somewhat: (1) additional power for pumps and fans; (2) spent acid solution could not be used as a water wash on the filters; so the wasting of the recovery-plant tails has necessitated pumping 2000 tons (328,340 U. S. gal.) more water from the mine each day.

The estimated recovery and actual recovery placed against the estimated cost and actual cost as of a recent month were as follows, based on a saving of 0.927 kg. (2.04 lb.) of KCN @ 50 cvs. per kg. (11.4 c. per lb.):

| | Estimate | | Actual | |
|---|---|---|---|---|
| | Centavos | Cents | Centavos | Cents |
| Value of KCN recovered | 46.35 | 23.17 | 48.22 | 24.11 |
| Costs | 14.56 | 7.28 | 16.65 | 8.33 |
| Net profit | 31.79 | 15.89 | 31.57 | 15.78 |

In other words, the total daily profit approximates ₱ 500 ($250).

## Suggestions for Erecting and Operating Cyanide-recovery Plants

1. The acidifier discharge should flow by gravity rather than be pumped to the top of the first disperser; in fact, it would be better if this discharge flowed by gravity through all of the dispersers and then to the clarifying filter if one is used, by gravity. This system would eliminate all pumps excepting the clarifier vacuum or centrifugal pump handling the acid solution drawn off through the filter leaves.

2. Dipping parts or painting steel acidifiers, dispersers and absorbers in hot asphalt is better than any antacid paint.

3. Acidifiers, dispersers and absorbers should be built of wood, square in section and with double walls with heavy tarred roofing paper between. These would cost less than steel or concrete and the upkeep would be much less.

4. An economic balance between the sulfur burned and the cyanide dispersed must be determined for any given dispersion and absorption capacity.

5. Exhaust-fan connections at the acidifiers and the stack into which the fan discharges should be of wood instead of wrought iron or steel. If acidifiers are of wood, the $SO_2$ entering them should first be cooled.

6. Although elemental sulfur is the simplest source of $SO_2$, it is expensive. A supply of gas sufficiently rich and constant can be obtained by roasting sulfide ores or concentrates. The circumstances might be such that sulfur for the recovery plant would cost little if anything. At Fresnillo, the sulfur from roasting iron concentrates is supplying $SO_2$ to the plant.

7. Under some conditions it might pay to conduct stack gases to a simple scrubber requiring no power and easy to clean. The scrubber could discharge into the storage tank feeding the acidifiers.

8. Dispersion is adversely affected by low temperatures, as during cold nights and in cold climates. Therefore, if feasible, although it was not at Santa Gertrudis, it will be found profitable to heat the solution before dispersion. (This is done at the Tonopah Extension mill, Nevada, where the Halvorsen process is employed.) If the solution is charged with lime, heating may cause trouble by precipitating out, as mentioned in this paper.

9. For the best dispersion results the last disperser discharge should always be distinctly acid to methyl orange. Each unit should consist of one disperser, one absorber and one fan, preferably of wood and square in cross-section.

10. Where a recovery plant is installed to treat barren mill solution it may be possible to operate without a filter for clarifying the spent acid solution; although under some conditions, even where silver is absent, such a filter would be necessary. When the solution contains much

copper it may be advantageous to filter it out for shipment to the smelter; then the clarified acid solution may be used direct as a water wash, first made alkaline with lime and then used on the filters, or it may be wasted if plenty of fresh water is available.

11. In treating barren plant solutions for the purpose of removing fouling agents such as copper and zinc; or for reducing the volume of mill solution so that a longer water wash can be given at the filters; or for the recovery of copper, silver and gold from solutions derived from the treatment of gold-silver ores containing too much copper for ordinary cyanidation and too little to smelt profitably, the following treatment scheme might work out to advantage.

*a.* If the copper minerals are oxidized and the copper content is too low to warrant a preliminary leach with $H_2SO_4$ or $H_2SO_3$, treat the ore with cyanide to recover the maximum amount of silver and copper. In the absence of gold, the silver could be precipitated with $Na_2S$ and the barren solution treated in a recovery plant and the spent acid solution filtered to remove the CuCNS then used in whole or in part as the sole and only filter wash, with the total wash effluent going back into the cyanide circuit.

*b.* Where gold is present the pregnant solution should first be precipitated with zinc dust; the barren solution so produced treated in the recovery plant; the recovery-plant solution tails filtered in a Butters machine to remove the CuCNS, and the filtered solution run into a small agitator containing lime, then into a thickener whose overflow would be used as the only filter wash as in the case where gold is absent. In both of these cases, some water would have to be added as a filter wash in order to make up for the solution lost with the final tailing filter cake.

*c.* The above scheme of treating silver-copper-gold ores by the cyanide process in combination with a recovery plant is entirely feasible from a metallurgical standpoint, at least, but whether a return will be made during the life of the mine, commensurate with the capital invested, is a problem that can be solved only by a study of the particular mine.

*d.* For instance, where a low-grade copper-silver orebody is owned by a smelting company it would appear, when the orebody is not too distant from the smelter, that the treatment of such an ore by cyanidation followed by the treatment of either the pregnant or the barren solution by the cyanide-recovery process would offer the cheapest and most logical method of attack. The reason for this is the fact that the largest expense in the operation of the recovery plant is the item of sulfur for the production of $SO_2$—a waste product of the smelter. Also, it might be advisable to give the ore a preliminary treatment with $SO_2$ for the purpose of extracting as much copper as possible before its contact with cyanide. This operation would also be free of cost in so far as the reagent itself is concerned.

*e.* Although all of the cyanide combined with the copper could be saved in the recovery plant, the higher the copper in the feed, the more cyanide is required in the cyanide-plant circuit. This would call for a larger recovery plant. A high cyanide in the cyanide-plant circuit would also require a longer filter wash in order to reduce mechanical filter losses to a minimum.

12. The actual operation of the plant requires the services of one man per shift. His time is spent feeding sulfur, taking samples and weir measurements hourly, noting and recording the amount of solution in the acidifier feed storage tank half-hourly, oiling pumps and fans, and looking after the plant in general. He also titrates the final disperser discharge hourly for acidity as a means of keeping the sulfur consumption within reason.

A boy is also kept on day shift, to titrate the acidifier feed and all the disperser discharges hourly. He calculates the percentage dispersions and posts the results for the burner operator. Although the titrating boy is not a necessity, his hourly results keep the operator alert and are also of assistance to the night man in that the latter, by looking over the day's results, can tell about what to expect in the way of recovery when running with a given acidity.

The greatest item in labor cost is the necessity of removing the lime from the acidifiers twice a month and cleaning absorber grids each month. Every 4 to 6 months the grids in No. 1 disperser must be removed; those in No. 2 will probably not have to be taken out oftener than once in 12 to 18 months. The sulfur burner and No. 9 fan are also cleaned monthly; also, the pumps are overhauled and, when necessary, are packed.

As the whole plant is working at maximum, and as Nos. 1 and 2 dispersers are operated as one unit, all jobs that would require a plant shutdown are postponed until the regular monthly stop of the cyanide plant.

13. Continual correspondence and personal contact was maintained with the cyanide-recovery plant at Fresnillo. This was mutually beneficial, and it is suggested that when other metallurgists are operating similar plants they should keep in touch with one another. The principle of this fairly new process is relatively simple, but the final mechanism of the plant has yet to be worked out.

## Acknowledgments

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especially its representative in Mexico, Luther Lennox, for valuable suggestions and assistance given during the early days of plant operation; also to Mr. Haun, representative at Fresnillo; to C. A. Lantz, general manager of Santa Gertrudis, for advice and criticism during the construction period and, further, for his permission to publish this article; to W. E. Crawford, mill superintendent, and M. S. Booth, assistant mill superintendent at Cia. Beneficiadora de Pachuca, for practical suggestions and assistance; and to the staff and men who helped during the many difficulties encountered in the new plant. L. G. Veale, drew the flow sheet and dispersers shown and other detailed plans and graphs which had to be omitted from this paper.

To Hugh Rose, managing director of the Santa Gertrudis Co., a great deal of credit is due for the pioneering spirit shown through his authorization of the construction of the first two large-size recovery plant units in Mexico—a 3000-ton plant at Fresnillo and a 2000-ton plant at Pachuca.

The manuscript was edited and condensed to about one-half its original length by M. W. von Bernewitz, secretary of the Milling Committee of the Institute. He also prepared the bibliography.

## Selected Bibliography

Following is a list of the most important papers on regeneration or recovery of cyanide, arranged chronologically. Doubtless other publications contain references to regeneration, but these have not been indexed under that head in the bound volumes and to find them would require considerable search; also, certain texts were unavailable to the compiler:

1. G. A. Packard: The Cyanide Process in the United States. *Trans.* A. I. M. E. (1896) **26,** 709–721.
2. H. Van F. Furman: Laboratory Tests in Connection with the Extraction of Gold from Ores by the Cyanide Process. *Trans.* A. I. M. E. (1896) **26,** 721–734.
3. S. B. Cristy: The Solution and Precipitation of the Cyanide of Gold. *Trans.* A. I. M. E. (1896) **26,** 735–772.
4. Discussion of papers 1, 2, 3. *Trans.* A. I. M. E. (1897) **27,** 821–846.
5. Charles Butters in 1903 used electrolytic precipitation at Virginia City, Nevada, and at Minas Prietas, Mexico, and profitable regeneration of cyanide resulted.
6. A. F. Crosse: Regeneration of Working Cyanide Solutions. *Eng. & Min. Jnl.* (1903) **75,** 817–818. (Abstracted from *Jnl.* Chem. Met. & Min. Soc. of So. Africa, March, 1903.) Tells of tests made during 1899.
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## DISCUSSION

R. R. Bryan, Pachuca, Hgo., Mexico (written discussion).—Cyanide regeneration or recovery? The terms are not synonymous. Regeneration implies a preceding degeneration; recovery implies a preceding loss. Cyanide degenerated would be lost, but all cyanide loss need not be through degeneration.

Cyanide losses have been generally divided into chemical and mechanical. The chemical loss is that occasioned through the degeneration or conversion of cyanide to a useless form such as the formation of sulfocyanates, cyanates, ferrocyanides, etc. The mechanical loss is that occasioned through incomplete removal of the useful cyanide from the tailings.

Regeneration is a term that can apply only to a recovery of the chemical loss. Recovery is a term that might apply to either chemical or mechanical loss. Since, however, regeneration confines itself to the chemical loss, it would seem expedient to understand recovery as only a recovery of the mechanical loss.

Mr. Lawr has described a cyanide recovery process which consists in a certain application of a cyanide transferal process to the problem of reducing the former mechanical loss. He improperly terms this transferal process the Mills-Crowe process. It is worthy of note that this transfer process described by Mr. Lawr may

be applied in other manners to the problem of recovering the mechanical loss and perhaps regenerating some of the chemical loss, especially where there has been serious fouling of solution by copper.

An example of another way to apply this cyanide transferal process is seen in the scheme employed at the Fresnillo unit of the Mexican Corpn. This company is controlled by the same interests that control the Cia Beneficiadora de Pachuca, whose operations Mr. Lawr has described.

The Fresnillo mill treats all of the solution for barren wash to this cyanide transferal process, absorbing the transferred cyanide in mill solution. The washing on the filter is then performed with this impoverished barren solution instead of with the former barren solution of high cyanide content. The result is that cyanide values as well as precious-metal values are effectively removed from the filter cake, which is discharged with a very low mechanical loss of cyanide.

It will be interesting to make some sort of comparison of these two distinct applications of a cyanide transferal process. This comparison might better be made by those in closer touch with these operations, but I will attempt to give impressions gained through having seen both and talked with the men operating them, and from a long study of the cyanide recovery and regeneration problems.

Concerning the recovery of the mechanical loss of cyanide, either scheme is efficient and both can recover upward of 80 per cent. of the mechanical loss. In the operation of either scheme, the character of the mill solution is changed by lesser additions required of new cyanide, which reduces the amount and character of salts in solution. Where fresh cyanide is added in form of white cyanide, this effect is less than when surronide is used. Surronide contains about 50 per cent. sodium chloride. Reducing amount of surronide added to mill solutions decreases their content in sodium chloride and lessens their corrosive action. This change in salt content of solutions may greatly affect the settling and filtering rate of the pulp.

In obtaining this effect the Fresnillo scheme goes further than the Santa Gertrudis scheme, in that it provides a certain amount of bleeding of mill solutions after transferal of their cyanide content. This bleeding tends to reduce salt concentrations. Not all the solution treated at Fresnillo is bled from circuit, as a considerable amount reenters through the filters.

During the cyanidation of an ore a great many salts form in the mill solution from its contact with ore and from zinc precipitations and these salts build up through cyclic use of the solutions. Their final concentration is determined by the amount of solution bled from the circuit. Generally this amount of solution bled from the circuit is held to a minimum to avoid undue loss of cyanide and consists only of the necessary loss of solution through the filter plant discharge. At some mills, the building up of detrimental salts has been such as to seriously interfere with operations and require a bleeding of plant solution. It is probable that most mills would receive considerable benefit through the cleansing effect of greater bleeding.

It is apparent that the Santa Gertrudis scheme can claim no advantage for cleaning solutions through bleeding and that to a greater or less extent the Fresnillo scheme has the advantage of this feature. Since the Santa Gertrudis scheme provides for additional filtering, it has the advantage of increased silver extraction, as described in Mr. Lawr's paper.

In a consideration of the economics of the two schemes, two parts should be mentioned: (1) capital costs and (2) operating costs.

In point of capital cost the Fresnillo scheme is much to be preferred, as it requires for its operation only the creation of a cyanide transferal plant. In addition to this, the Santa Gertrudis scheme requires increased and usually costly filter equipment to obtain the prolonged water wash which is to form the solution from which cyanide is to be transferred. My impression is that cyanide transferal equipment will cost

from $8 to $14 per ton capacity of solution treated and that additional filter equipment required by the Santa Gertrudis scheme will cost from $8 to $12 per ton capacity solution obtained. Good practice in either case indicates that one ton of solution should be treated per ton ore milled.

In point of operating cost, the Santa Gertrudis scheme is much more economical, because every unit of cyanide transferred represents a unit of cyanide actually saved, whereas in the Fresnillo scheme it is necessary to transfer three or four units of cyanide for each unit actually saved. The greatest operating cost of the transferal process is for sulfur and required consumption depends both on amount of cyanide to be transferred and amount of alkalinity in solution to be neutralized. This objection to the Fresnillo scheme has been overcome very cleverly at that plant by obtaining free $SO_2$ through the roasting of a pyrite concentrate, an operation that is economical within itself. Other plants might not be so fortunately situated.

The Real del Monte Co. at its Guerrero mill for a number of years has operated still another variation in the application of this transferal scheme. The tailings from the cyanide plant are conveyed several kilometers to the tailings site, where they are carefully stacked and solution is recovered both through decantation and percolation. A considerable quantity of silver is extracted from the tailings by percolation and also in the course of travel to the tailings site and during disposal thereon. This silver is recovered by precipitation in zinc boxes and the solution tails from these boxes are then subjected to the cyanide transferal process, with absorption of the cyanide in a milk of lime solution. The result is a concentrated solution carrying 30 kg. of cyanide per ton solution. This concentrated solution is pumped back to the mill circuit at Guerrero mill. Cyanide recovery schemes at this mill would have recovered much more cyanide than the scheme employed, but would have made impossible the silver leaching and recovery at the tailings dam.

The Real del Monte plant, at its enlarged Loreto mill, has just completed the largest and latest cyanide transferal plant in existence. This plant will eventually operate upon a scheme different from any mentioned heretofore, which is in part a modification of both the Santa Gertrudis and Fresnillo schemes. One-third of the solution treated will be plant barren solution and two-thirds will be obtained from an extra water wash in filters. As far as possible, after the cyanide has been transferred all of the solution will be wasted, and every effort will be made to avoid reentrance of this solution into the mill solutions.

# Effect of Copper and Zinc in Cyanidation with Sulfide-acid Precipitation*

By E. S. Leaver† and J. A. Woolf,‡ Reno, Nev.

(San Francisco Meeting, October, 1929)

The presence of soluble base metals in precious-metal ores usually precludes cyanidation as the best method of treatment. The laboratory experiments described in this paper show the possibility of cyanidation of gold-silver ores containing less than 0.5 per cent. of cyanide-soluble copper and the effect of zinc in the cyanide solution.

## Part I.—Copper in Cyanidation

The proposed process of cyanidation of precious-metal ores containing copper is based on the regeneration of about 80 per cent. of the cyanide used in the dissolution of the copper. The method of regeneration involves a combination of the sulfide and the acid precipitation of the copper and silver. The resultant solution is made alkaline with lime, and the gold is precipitated with zinc dust.

### *Solubility of Copper Minerals in Cyanide Solution*

In order to determine the solubility of copper minerals, including metallic copper, under the usual conditions for cyanidation, experiments were conducted with synthetic ores. Each ore sample was prepared by mixing the particular pure copper mineral with barren sea sand. Both the mineral and sand were ground to pass 100 mesh before they were thoroughly mixed. The percentage of copper in each head sample was determined by direct assay, excepting the metallic copper sample, which was computed on weights before mixing. Table 1 gives the results.

Azurite, bornite, chalcocite, cuprite, malachite and finely divided metallic copper are readily and completely soluble under the usual conditions for cyanidation. Enargite and tetrahedrite are sufficiently soluble to cause an excessive loss of cyanide, and they also cause fouling of solutions with arsenic and antimony. Precious-metal ores containing small percentages of chalcopyrite or chrysocolla may give satisfactory returns with the usual cyanidation.

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*Ratio of Cyanide Used to Copper Dissolved from Various Minerals*

The chemical reactions involved in the cyanide dissolution of copper from copper minerals are complex and vary with the different minerals. From the plant standpoint the important consideration is the amount of the active cyanide solvent that is used in the mill solution for the dissolution of copper. Table 2 gives the ratio of cyanide used to the copper dissolved from each mineral.

The ratio of cyanide used to copper dissolved varies for each of the minerals given. It corresponds approximately to an average molecular

TABLE 1.—*Solubility of Copper Minerals and Metallic Copper in Cyanide Solution*

Ratio of solution to ore, 10:1. Strength of solution used, 2 lb. NaCN, lime equivalent to 10 lb. per ton of ore added to pulp in each case. Treatment, 24 hr. at 45° C.

| Mineral | Assays, Percentage of Copper | | Extraction, Percentage of Copper | Remarks |
|---|---|---|---|---|
| | Heads | Tailing[a] | | |
| Azurite | 0.254 | None | 100.0 | |
| Bornite | 0.264 | Trace | 99.0+ | Small amount soluble sulfides in solution. |
| Chalcocite | 0.244 | None | 100.0 | |
| Chalcopyrite | 0.497 | 0.456 | 8.2 | |
| Chrysocolla | 0.254 | 0.214 | 15.7 | |
| Cuprite | 0.234 | None | 100.0 | |
| Enargite | 0.213 | 0.053 | 75.1 | Small amounts of soluble sulfides and arsenic in solution. |
| Malachite | 0.244 | None | 100.0 | |
| Tetrahedrite | 0.183 | 0.103 | 43.7 | Trace of antimony in solution. |
| Metallic copper[b] | 0.267 | None | 100.0 | |

[a] Tailing assays checked by solution assays.
[b] Air admitted during dissolving.

ratio of 3 to 1. The higher loss shown for enargite is in part due to dissolution of arsenic. The loss for tetrahedrite is also higher than the average, due to dissolution of antimony. The low loss for cuprite and the lowest loss for metallic copper are probably explained by the reactions that do not include the formation of cyanates or the least amount of complex cyanide compounds. These results were obtained with pure minerals and clean solutions. With mill solutions and complex ores any factors tending to increase the amount of complex cyanide salts would correspondingly increase the loss of cyanide.

TABLE 2.—*Ratio of Cyanide Used to Copper Dissolved from Various Copper Minerals*

| Mineral | Ratio of NaCN Loss to Copper Dissolved, Pounds |
|---|---|
| Azurite | 2.28:1 |
| Bornite | 2.27:1 |
| Chalcocite | 2.38:1 |
| Chalcopyrite | 2.44:1 |
| Chrysocolla | 2.25:1 |
| Cuprite | 2.01:1 |
| Enargite | 2.75:1 |
| Malachite | 2.42:1 |
| Tetrahedrite | 2.50:1 |
| Metallic copper | 1.84:1 |

*Effect of Copper in Cyanide Solutions on Gold and Silver Extraction*

Solutions containing different amounts of copper were prepared by dissolving malachite in sodium cyanide solution. This dissolution was carried on until only a little free cyanide remained, as indicated by titration with silver nitrate. Sodium cyanide salt was then added to the solution to increase the free cyanide content, after which the solutions were used to treat a gold-silver ore by agitation. Table 3 gives a comparison of the extraction obtained by use of a clean solution with that obtained with solutions containing copper.

TABLE 3.—*Effect of Copper in Cyanide Solutions on Gold and Silver Extraction*

Heads assayed 10.29 oz. Ag and 0.56 oz. Au. Ratio of solution to ore, 3:1. Treatment 24 hr. at 45° C.

| Experiment Number | Solution Titrations, Pounds per Ton | | | | Copper in Solution, Per Cent. | Tailing Assay, Ounces per Ton | | Extraction, Per Cent. | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| | On | | Off | | | | | | | |
| | Free NaCN | CaO | Free NaCN | CaO | | Ag | Au | Ag | Au | |
| 1 | 4.25 | 0.20 | 3.55 | 1.30 | None | 0.77 | 0.030 | 92.6 | 94.7 | Used a clean solution containing no copper. |
| 2 | 4.10 | 0.70 | 3.10 | 2.10 | 0.101 | 0.88 | 0.025 | 91.5 | 95.5 | Used sodium-copper cyanide solution, containing free cyanide. |
| 3 | 4.40 | 1.20 | 3.60 | 1.80 | 0.218 | 0.87 | 0.025 | 91.7 | 95.5 | Used sodium-copper cyanide solution containing free cyanide |

The presence of copper in amounts up to 4 lb. per ton of solution has no detrimental effect on the extraction of gold and silver in the cases shown. Additional experiments indicate that the copper may be increased to 10 lb. per ton of solution without affecting its efficacy as a solvent for precious metals, provided that the solution contains free cyanide equal to the quantity needed in fresh solution to obtain maximum extraction.

### *Dissolving Efficacy of Sodium-copper Cyanide Solution*

Solutions were prepared by treating malachite with a sodium cyanide solution until no more copper would go into solution. Even at this point there invariably remained a small amount of free cyanide in the solution, as shown by titration with silver nitrate. These solutions containing varied amounts of sodium-copper cyanide were used in the treatment of a gold-silver ore known to yield good extraction with clean sodium cyanide solution. Table 4 gives the results of these experiments.

The sodium-copper cyanide solution formed by the dissolution of malachite in sodium cyanide is a weak solvent for the precious metals. The dissolving effect of this solution is roughly proportional to the time of contact. It is also noted that the pregnant copper cyanide solution generally shows a small amount of free cyanide, which indicates that the double cyanide is slightly dissociated. This dissociation closely follows the time of contact and the dissolution of the precious metals. Excess lime does not increase the extraction of precious metals but an excess of caustic soda greatly increases gold extraction, and to a lesser extent favorably affects silver extraction over a 24-hr. period.

### *Removal of Copper from Solution, and Regeneration of Combined Cyanide*

Although the presence of copper in cyanide solution, in amounts not exceeding 4 or 5 lb. per ton, does not appear to affect adversely the extraction of gold and silver when sufficient free cyanide is present, it is necessary that the copper be removed to prevent excessive accumulation. Also from the cost standpoint, the cyanide combined with the copper must be released for re-use in dissolving precious metals.

Zinc will precipitate the copper almost completely after several hours agitation, provided there are 3 to 4 moles of free cyanide present for each mole of copper. The zinc replaces the copper, thus forming the double sodium-zinc cyanide, which in the presence of excess free alkali is a weak solvent for gold and silver. Experiments described in Part II of this paper show that the accumulation of zinc in the solution from this precipitation tends to lower the extraction of the precious metals, and that if maximum extraction is to be maintained either the zinc must be removed from the solution or some other method of precipitating the

TABLE 4.—*Dissolving Efficacy of Sodium-copper Cyanide Solution*

Ratio of solution to ore, 3:1. Treatment, 24 hr. at 45° C.

| Experiment Number | Solution Titrations, Pounds per Ton | | | | Period of Treatment, Hours | Copper in Solution, Per Cent. | Assays, Ounces per Ton | | | | Extraction, Per Cent. | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | On | | Off | | | | Heads | | Tailings | | | | |
| | Free NaCN | CaO | Free NaCN | CaO | | | Ag | Au | Ag | Au | Ag | Au | |
| 1 | 4.25 | 0.2 | 3.55 | 1.30 | 24 | None | 10.29 | 0.56 | 0.77 | 0.03 | 92.6 | 94.7 | Used a fresh solution containing no copper. |
| 2 | 0.24 | 0.3 | None | 1.80 | 24 | None | 10.50 | 0.65 | 10.26 | 0.34 | 2.3 | 47.7 | Used very dilute solution containing no copper. |
| 3 | 0.20 | 0.75 | Trace | 2.00 | 24 | 0.101 | 10.50 | 0.65 | 9.10 | 0.37 | 13.3 | 43.2 | Added excess lime to the ore charge. Used solution containing copper. |
| 4 | Trace | 2.00 | None | 2.20 | 24 | 1.006 | 10.50 | 0.65 | 9.89 | 0.36 | 5.8 | 44.5 | Re-use pregnant solution from experiment 3. Added excess lime to ore charge. |
| 5 | 0.20 | 1.10 | 0.10 | None | 24 | 0.218 | 10.29 | 0.56 | 9.17 | 0.28 | 10.9 | 50.0 | No lime added to ore charge. Used solution containing copper. |
| 6 | 0.20 | 1.10 | 0.30 | 1.90 | 24 | 0.218 | 10.29 | 0.56 | 9.18 | 0.32 | 10.8 | 42.8 | Added excess lime to ore charge. |
| 7 | 0.20 | 1.10 | 0.20 | 1.40 | 48 | 0.218 | 10.29 | 0.56 | 8.75 | 0.30 | 14.9 | 46.4 | Added excess lime to ore charge. |
| 8 | 0.20 | 1.10 | None | 1.10 | 72 | 0.218 | 10.29 | 0.56 | 7.15 | 0.26 | 30.6 | 53.6 | Added excess lime to ore charge. |
| 9 | 0.20 | 1.10 | Trace | 10.5 | 24 | 0.218 | 10.29 | 0.56 | 8.03 | 0.07 | 22.0 | 87.3 | Added excess caustic soda to ore charge. |

TABLE 5.—*Precipitation of Copper from Cyanide Solution with Sodium Sulfide and Sulfuric Acid*

Showing percentage of cyanide regenerated, based on total amount used during dissolution of the copper.

| Experiment Number | Method of Treatment[a] | Solution Analyses | | | | | | | Copper Precipitated, Per Cent. | Cyanide Regenerated, Percentage of Total Amount Used | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Original Solution | After Dissolving Copper | | | After Precipitating Copper and Regenerating Cyanide | | | | | |
| | | NaCN, Pounds per Ton | NaCN, Pounds per Ton | CaO, Pounds per Ton | Cu, Per Cent. | NaCN, Pounds per Ton | CaO, Pounds per Ton | Cu, Per Cent. | | | |
| 1 | Add calculated amount of $Na_2S$ sufficient to precipitate 80 per cent. of the copper. Make just neutral with $H_2SO_4$. Filter and make filtrate alkaline with lime. Experiment was conducted in open apparatus. | 8.30 | 2.90 | 0.5 | 0.12 | 2.50 | 1.7 | 0.065 | 45.8 | −7.4 | No copper precipitated in alkaline solution. Copper precipitation incomplete in neutral solution. Soluble sulfides left in solution. Negative cyanide regeneration, due to escape of HCN gas. |
| 2 | Add enough $Na_2S$ to precipitate all of the copper. Make acid with $H_2SO_4$. Filter and make filtrate alkaline with lime. Experiment was conducted in open apparatus. | 8.30 | 3.30 | 1.0 | 0.10 | 5.50 | 1.5 | 0.002 | 98.0 | 44.0 | Copper precipitation complete in acid solution. Cyanide regeneration low, due to loss of HCN gas. No soluble sulfides in solution. |
| 3 | Treat just as in experiment 2, except that precipitation is done in closed apparatus. Filtration was in open funnel. | 8.20 | 3.00 | 2.0 | 0.11 | 6.40 | 1.4 | 0.002 | 98.0 | 65.4 | Increase in percentage of cyanide regenerated as less HCN is lost during manipulation. No soluble sulfides left in solution. |
| 4 | Precipitate as in experiment 3. Filter and catch filtrate in strong lime water. Entire experiment was conducted in closed apparatus. | 6.00 | 1.10 | 0.45 | 0.097 | 5.30 | 2.20 | 0.001 | 99.0 | 85.5 | High percentage cyanide regeneration because no loss of HCN. No soluble sulfides in solution. |
| 5 | Treatment same as experiment 4..... | 3.90 | 1.20 | 1.1 | 0.055 | 3.46 | 1.60 | 0.001 | 98.0 | 83.4 | No soluble sulfides left in solution. |
| 6 | Make solution acid with $H_2SO_4$; then add calculated amount $Na_2S$ to precipitate all of the copper. Filter and catch filtrate in strong limewater. Entire experiment was conducted in closed apparatus. | 3.90 | 1.20 | 1.1 | 0.055 | 3.46 | 1.60 | 0.001 | 98.0 | 83.4 | Precipitate formed by the $H_2SO_4$ was decomposed and precipitated as sulfide upon addition of $Na_2S$. No soluble sulfides left in solution. |

[a] All treatment conducted at normal room temperature, approximately 23° C.

copper must be employed. Magnesium dust was tried as a precipitant under varied conditions of time, temperature, alkalinity and acidity. The results were negative from the standpoint of plant application.

In the following experiments the desired quantities of copper in the solution were obtained by treating malachite with sodium cyanide solution containing free alkali in the form of lime at normal room temperature. The copper was then precipitated with sodium sulfide and sulfuric acid. The amount of cyanide regenerated was determined by titration with silver nitrate at various steps in the procedure. Table 5 shows what happened.

Sodium sulfide is not a precipitant for copper from an alkaline cyanide solution; it is an effective precipitant if the solution is acidified. The hydrocyanic acid formed is very soluble at temperatures below 26° C., but some of it will readily escape from solutions in open containers, especially if the solution is subjected to agitation. It is necessary to make provision for retaining this gas until the precipitate has been removed and the solution made alkaline. This may be accomplished by the use of closed apparatus. Details of a proposed apparatus will be given in a *Technical Paper* now being prepared by the U. S. Bureau of Mines.

The consumption of sodium sulfide is proportional to the amount of copper precipitated. In the foregoing experiments, where 98 per cent. or more of the copper was precipitated, the consumption of sodium sulfide averaged about 0.7 lb. (calculated on a basis of 100 per cent. $Na_2S$) per pound of copper precipitated. The acid consumption depends on the strength of the original solution in both cyanide and lime. In the tests shown it varied from 4.5 to 6.5 lb. of sulfuric acid per pound of copper precipitated.

### *Cyanide Loss as Cyanates*

Any cyanide combined to form cyanate during the dissolution of copper will not be regenerated as free cyanide by this method. Pure potassium cyanate (KCNO) was prepared in the laboratory. This was dissolved in water and the resultant solution treated with sodium sulfide and sulfuric acid as in the experiments described. No precipitate was formed and the solution contained no free cyanide as indicated by titration with silver nitrate.

### *Dissolving Efficacy of Regenerated Solutions*

A fresh sodium cyanide solution titrating 4.9 lb. NaCN was prepared and used to dissolve copper from malachite until saturated. The resultant solution was used in the treatment of an ore under the different conditions shown in Table 6.

TABLE 6.—*Dissolving Efficacy of a Regenerated Solution*

The sodium-copper cyanide solution contained 0.2 lb. free cyanide and 0.101 per cent. copper. Heads assayed 10.89 oz. Ag., 0.56 oz. Au. Ratio of solution to ore, 3:1. Treatment, 24 hr. at 45° C.

| Experiment Number | Solution Analyses | | | | | Tailing Assay, Ounces per Ton | | Extraction, Per Cent. | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| | On | | | Off | | | | | | |
| | Free NaCN, Pounds per Ton | CaO, Pounds per Ton | Cu, Per Cent. | Free NaCN, Pounds per Ton | CaO, Pounds per Ton | Ag | Au | Ag | Au | |
| 1 | 4.25 | 0.2 | None | 3.55 | 1.30 | 0.80 | 0.030 | 92.6 | 94.7 | Used a clean cyanide solution containing no copper. |
| 2 | 4.10 | 0.7 | 0.101 | 3.10 | 2.10 | 0.93 | 0.025 | 91.5 | 95.5 | Used the sodium-copper cyanide solution after addition of more sodium cyanide. |
| 3 | 3.40 | 2.0 | 0.002 | 2.40 | 2.50 | 0.83 | 0.025 | 92.3 | 95.5 | Copper in the sodium-copper cyanide solution was precipitated by sulfide-acid method, and the regenerated solution used. |

A comparison of the foregoing experiments shows that the regenerated solution is as active as a fresh cyanide solution in the dissolution of the precious metals.

Several series of experiments were made with precious-metal ores containing soluble copper, in which the dissolved metals were precipitated and the solution regenerated at the end of each cycle; the regenerated solution was used in the following cycle. Enough sodium cyanide salt was added to the barren solution each time to keep the solution strength about constant. Table 7 gives results from one set of these experiments, with an ore to which malachite had been added.

An average of a little more than 80 per cent. of the total cyanide used during the dissolving period was regenerated. The regeneration figures are based on solution titrations. These figures are substantiated by the fact that the amounts of cyanide added at the end of each cycle were calculated and checked by titrations. The extractions are nearly constant through the entire series, showing that the regenerated solution retains its efficacy as a solvent for copper and precious metals.

### *Application of Proposed Process to Ores That Give Unsatisfactory Recovery*

The application of the proposed process to ores that do not give satisfactory recovery by the usual methods is shown by the following examples:

1. Oxidized siliceous gold-silver ore from the Buffalo Valley mine near Valmy, Nev., contains a small amount of copper. Most of the

TABLE 7.—*Experiments Using Sodium Sulfide and Sulfuric Acid as Precipitants*

Heads assayed 10.69 oz. Ag, 0.56 oz. Au, 0.98 per cent. Cu. Ratio of solution to ore, 10:1. Treatment, 24 hr. at 45° C.

| Cycle Number | Solution Titrations, Pounds NaCN per Ton | | | Cyanide Loss, Pounds NaCN per Ton Ore | | Cyanide Regenerated | | Precipitation Reagents | | | | Metals Precipitated by Sulfide-acid Treatment,[a] Per Cent. | | | Tailing Assay | | | Extraction, Per Cent. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | On | Off | After Regeneration | Before Regeneration | After Regeneration | Pounds per Ton Ore | Percentage of Total | Pounds per Ton Ore | | Pounds per Pound Copper Precipitated | | Ag | Au | Cu | Ag, Ounces per Ton | Au, Ounces per Ton | Cu, Per Cent. | Ag | Au | Cu |
| | | | | | | | | $Na_2S$ | $H_2SO_4$ | $Na_2S$ | $H_2SO_4$ | | | | | | | | | |
| 1 | 6.60 | 1.75 | 5.50 | 48.5 | 11.0 | 37.5 | 77.3 | 14.6 | 82.9 | 0.81 | 4.6 | 100.0 | 26.6 | 95.8 | 0.88 | 0.025 | 0.04 | 91.7 | 95.5 | 95.9 |
| 2 | 6.30 | 1.30 | 5.50 | 50.0 | 8.0 | 42.0 | 84.0 | 15.2 | 96.0 | 0.76 | 4.8 | 100.0 | 14.8 | 100.0 | 0.88 | 0.025 | 0.02 | 91.7 | 95.5 | 97.9 |
| 3 | 6.20 | 1.20 | 5.20 | 50.0 | 10.0 | 40.0 | 80.0 | 15.6 | 140.0[b] | 0.84 | 7.5[b] | 100.0 | 16.9 | 98.0 | 0.96 | 0.015 | 0.03 | 91.0 | 97.0 | 96.9[b] |
| 4 | 5.90 | 1.28 | 4.90 | 46.2 | 10.0 | 36.2 | 78.3 | 15.6 | 81.5 | 0.82 | 4.3 | 100.0 | 9.1 | 98.0 | 0.93 | 0.035 | 0.01 | 91.3 | 93.8 | 99.0 |
| 5 | 6.20 | 1.38 | 5.38 | 48.2 | 8.2 | 40.0 | 83.0 | 15.2 | 81.5 | 0.80 | 4.3 | 100.0 | 11.2 | 99.0 | 0.98 | 0.030 | 0.01 | 90.8 | 94.7 | 99.0 |
| Avg... | 6.24 | 1.38 | 5.30 | 48.6 | 9.4 | 39.2 | 80.6 | 15.2 | 96.4 | 0.81 | 5.1 | 100.0 | 15.7 | 98.2 | 0.93 | 0.026 | 0.02 | 91.3 | 95.3 | 97.9 |

[a] Gold not precipitated by the sulfide-acid treatment was precipitated with zinc dust after regeneration of the cyanide solution.

[b] High $H_2SO_4$ consumption due to high alkalinity of solution.

copper occurs as chrysocolla which is not very soluble in cyanide solution (see Table 1).

Cyanidation is the present recovery method. In mining an attempt is made to select the ores most free from copper, but often the cyanide loss caused by copper is excessive.

2. The Tenabo Consolidated Mines Co., about 40 miles south of Beowawe, Nev., mines a siliceous ore containing pyrite and arsenopyrite. The copper occurs mostly as chrysocolla and malachite; gold is the principal constituent of value. The present milling, amalgamation and flotation does not give a high recovery of the gold.

3. The Douglas tailings resulted from the various treatment methods used on the original Comstock ore and present a difficult retreatment

TABLE 8.—*Experiments with Different Ores Using*

| Ore Used, Treatment and Ratio of Solution to Ore | Head Assay | | | Cycle Number | Solution Titrations, Pounds NaCN per Ton | | Cyanide Loss, Pounds NaCN per Ton Ore | | Cyanide Regenerated | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ag, Ounces per Ton | Au, Ounces per Ton | Cu, Per Cent. | | On | Off | Before Regeneration | After Regeneration | Pounds per Ton Ore | Per Cent. of Total |
| Buffalo Valley Mines Co., Valmy, Nev. Treatment, 24 hr. at 23° C. Ratio of solution to ore, 6:1. | | | | 1 | 1.96 | 0.92 | 6.24 | | | |
| | | | | 2 | 1.92 | 1.10 | 4.92 | | | |
| | | | | Avg. of cycles 1 and 2 | 1.94 | 1.00 | 5.58 | 1.20 | 4.38 | 78.6 |
| | | | | 3 | 2.16 | 1.26 | 5.40 | | | |
| | | | | 4 | 2.12 | 1.26 | 5.16 | | | |
| | | | | Avg. of cycles 3 and 4 | 2.14 | 1.26 | 5.28 | 1.26 | 4.02 | 76.2 |
| | 1.29 | 0.38 | 0.68 | Avg. of four cycles | 2.04 | 1.13 | 5.43 | 1.23 | 4.20 | 77.4 |
| Tenabo Cons. Mines Co., Beowawe, Nev. Treatment, 24 hr. at 23° C. Ratio of solution to ore, 6:1. | | | | 1 | 1.96 | 1.04 | 5.52 | | | |
| | | | | 2 | 1.88 | 1.02 | 5.16 | | | |
| | | | | Avg. of cycles 1 and 2 | 1.92 | 1.03 | 5.34 | 1.14 | 4.20 | 78.6 |
| | | | | 3 | 2.10 | 1.20 | 5.40 | | | |
| | | | | 4 | 2.06 | 1.22 | 5.04 | | | |
| | | | | Avg. of cycles 3 and 4 | 2.08 | 1.21 | 5.22 | 1.18 | 4.04 | 77.7 |
| | 1.25 | 0.90 | 0.29 | Avg. four cycles | 2.00 | 1.12 | 5.28 | 1.16 | 4.12 | 78.2 |
| Douglas tailings, Dayton, Nev. Treatment, 24 hr. at 45° C. Ratio of solution to ore, 5:1. | | | | 1 | 1.96 | 1.36 | 3.00 | | | |
| | | | | 2 | 1.92 | 1.28 | 3.20 | | | |
| | | | | 3 | 2.00 | 1.30 | 3.50 | | | |
| | | | | 4 | 2.00 | 1.36 | 3.20 | | | |
| | | | | Avg. of cycles 1 to 4 | 1.97 | 1.325 | 3.23 | 0.73 | 2.50 | 77. |
| | | | | 5 | 2.70 | 2.00 | 3.50 | | | |
| | | | | 6 | 2.00 | 1.20 | 4.00 | | | |
| | | | | Avg. of cycles 5 and 6 | 2.35 | 1.60 | 3.75 | 0.80 | 2.95 | 78.7 |
| | 2.78 | 0.055 | 0.122 | Avg. of all 6 cycles | 2.097 | 1.417 | 3.40 | 0.75 | 2.65 | 77 8 |

problem. In addition to the remaining small gold and silver value, the tailings now contain copper and mercury introduced in former amalgamation treatment. They also contain organic matter introduced as refuse from Virginia City. The present recovery method is flotation to obtain a concentrate, from which mercury is recovered by retorting; the residues are shipped to the smelter for the recovery of the gold, silver and copper. Table 8 details the results of experiments made on these ores with sodium sulfide and sulfuric acid as precipitants.

The average percentage of cyanide regenerated in the treatment of these ores is approximately 78 per cent. In these ores, which contain low percentages of cyanide-soluble copper, the loss of cyanide due to copper bears a smaller ratio to the total cyanide loss than in ores contain-

*Sodium Sulfide and Sulfuric Acid as Precipitants*

| Precipitation Reagents | | | | Metals Precipitated by Sulfide-acid Treatment, Per Cent. | | | Tailing Assay | | | Extraction, Per Cent. | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pounds per Ton Ore | | Pound per Pound Copper Precipitated | | | | | | | | | | | |
| $Na_2S$ | $H_2SO_4$ | $Na_2S$ | $H_2SO_4$ | Ag | Au | Cu | Ag, Ounces per Ton | Au, Ounces per Ton | Cu, Per Cent. | Ag | Au | Cu | |
| | | | | | | | 0.79 | 0.040 | 0.548 | 38.8 | 89.5 | 19.4 | Metals were not precipitated at end of this cycle. |
| | | | | | | | 0.83 | 0.035 | 0.578 | 35.7 | 90.8 | 15.0 | Precipitated Ag and Cu with $Na_2S$ and $H_2SO_4$, then used zinc dust to precipitate gold. |
| 2.10 | 14.0 | 0.90 | 6.0 | 100.0 | 10.8 | 99.0 | 0.81 | 0.037 | 0.563 | 37.3 | 90.1 | 17.2 | |
| | | | | | | | 0.77 | 0.045 | 0.560 | 40.3 | 88.1 | 17.7 | Same as cycle 1. |
| | | | | | | | 0.78 | 0.040 | 0.584 | 39.5 | 89.5 | 14.1 | Same as cycle 2. |
| 1.90 | 13.0 | 0.90 | 6.0 | 100.0 | 8.2 | 99.0 | 0.77 | 0.043 | 0.572 | 39.9 | 88.8 | 15.9 | |
| 2.00 | 13.5 | 0.90 | 6.0 | 100.0 | 9.5 | 99.0 | 0.79 | 0.040 | 0.568 | 38.8 | 89.5 | 16.5 | |
| | | | | | | | 0.28 | 0.070 | 0.176 | 77.6 | 92.0 | 39.3 | Metals were not precipitated at end of this cycle. |
| | | | | | | | 0.29 | 0.070 | 0.188 | 76.7 | 92.0 | 36.2 | Precipitated Ag and Cu with $Na_2S$ and $H_2SO_4$, then used zinc dust to precipitate gold. |
| 1.9 | 14.0 | 0.90 | 6.5 | 100.0 | 9.6 | 99.0 | 0.29 | 0.070 | 0.182 | 77.2 | 92.0 | 37.2 | |
| | | | | | | | 0.32 | 0.068 | 0.180 | 74.3 | 92.5 | 37.9 | Same as cycle 1. |
| | | | | | | | 0.30 | 0.068 | 0.194 | 76.0 | 92.5 | 33.1 | Same as cycle 2. |
| 1.9 | 13.4 | 0.90 | 6.5 | 100.0 | 9.8 | 99.0 | 0.31 | 0.068 | 0.187 | 75.2 | 92.5 | 35.5 | |
| 1.9 | 13.7 | 0.90 | 6.5 | 100.0 | 9.7 | 99.0 | 0.30 | 0.069 | 0.184 | 76.2 | 92.3 | 36.4 | |
| | | | | | | | 0.35 | 0.0075 | 0.070 | 87.4 | 86.4 | 42.6 | Metals were not precipitated at end of this cycle. |
| | | | | | | | 0.36 | 0.0080 | 0.066 | 87.0 | 85.5 | 45.8 | Same as cycle 1. |
| | | | | | | | 0.36 | 0.0080 | 0.060 | 87.0 | 85.5 | 50.8 | Same as cycle 1. |
| | | | | | | | 0.40 | 0.0090 | 0.066 | 85.7 | 83.7 | 45.8 | Precipitated Ag and Cu with $Na_2S$ and $H_2SO_4$, then used zinc dust to precipitate gold. |
| 1.05 | 9.0 | 0.93 | 8.0 | 100.0 | 10.5 | 97.3 | 0.37 | 0.0081 | 0.066 | 86.8 | 85.3 | 46.3 | |
| | | | | | | | 0.35 | 0.0090 | 0.061 | 87.4 | 83.7 | 50.0 | Same as cycle 1. |
| | | | | | | | 0.40 | 0.0090 | 0.058 | 85.7 | 83.7 | 52.5 | Same as cycle 4. |
| 1.25 | 11.5 | 1.0 | 9.2 | 100.0 | 9.6 | 98.0 | 0.38 | 0.0090 | 0.060 | 86.6 | 83.7 | 51.3 | |
| 1.12 | 9.8 | 0.95 | 8.4 | 100.0 | 10.2 | 97.5 | 0.37 | 0.0084 | 0.064 | 86.7 | 84.8 | 48.0 | |

ing more copper. Again, the total cyanide regenerated is less because factors other than copper account for part of the loss.

For ores containing a small amount of copper, say 0.1 to 0.2 per cent. our experiments show that it is not necessary or even advisable to precipitate the metals from the solution after each cycle; every third or fourth cycle is often enough. The dissolved metals accumulate in solution but do not decrease the subsequent extraction of the precious metals.

Complex ores that contain a fractional percentage of copper necessarily show higher acid consumption per pound of copper precipitated, because the ratio of lime and cyanide to copper in the solution is greater. In these experiments the average loss of acid is approximately 7.0 lb. per pound of copper precipitated. The consumption of sodium sulfide is proportional to the amount of metals to be precipitated. In these tests it approximates 0.9 lb. of sodium sulfide per pound of copper precipitated.

The extraction of gold and silver remain nearly constant during the cyclic experiments for each ore. This shows that the regenerated solution is as effective a solvent as fresh solution.

## Part II.—Zinc in Cyanidation

All of the common zinc minerals are attacked under the usual conditions for cyanidation. Table 9 gives the percentage of zinc dissolved from each mineral.

Each head sample as given was prepared by mixing each pure zinc mineral with clean, barren sand, both previously crushed to 100 mesh.

Table 9.—*Solubility of Zinc Minerals in Cyanide Solution*

Strength of solution used, 3.95 lb. NaCN. Ratio of solution to ore, 5:1. Treatment, 24 hr. at 45° C.

| Mineral | Assays, Per Cent. Zinc | | Extraction, Per Cent. Zinc |
|---|---|---|---|
| | Heads | Tailings | |
| Sphalerite, $ZnS$ | 1.36 | 1.11 | 18.4 |
| Willemite, $ZnSiO_4$ | 1.22 | 1.06 | 13.1 |
| Hydrozincite, $3ZnCO_3.2H_2O$ | 1.36 | 0.87 | 35.1 |
| Calamine, $H_2Zn_2SiO_5$ | 1.19 | 1.03 | 13.4 |
| Franklinite, $\begin{pmatrix}Fe\\Zn\\Mn\end{pmatrix}O.\ \begin{pmatrix}Fe\\Mn\end{pmatrix}_2O_3$ | 1.19 | 0.95 | 20.2 |
| Zincite, $ZnO$ | 1.22 | 0.79 | 35.2 |
| Smithsonite, $ZnCO_3$ | 1.22 | 0.73 | 40.2 |

### *Solubility of Zinc Dust in Cyanide Solution*

It is known that zinc enters the mill cyanide solution in direct proportion to the metals which it precipitates. Additional zinc also

enters the mill solution by direct dissolution of the zinc dust used to precipitate the precious metals. Table 10 gives the rate of dissolution of zinc dust in a cyanide solution of the usual mill strength at normal room temperature.

TABLE 10.—*Solubility of Zinc Dust in Cyanide Solution*

Zinc dust all through 150 mesh and 96 per cent. through 200 mesh. 1200 c.c. of solution (2.9 lb. NaCN) and 0.5 g. zinc as zinc dust used in each experiment. Temperature during agitation, 23° C.

| Experiment Number | Lime Present, Pounds CaO per Ton Solution | Period of Agitation, Hours | Zinc in Solution after Agitation, Per Cent. | Zinc Dissolved | |
|---|---|---|---|---|---|
| | | | | Grams | Per Cent. |
| 1 | None | ¼ | 0.0157 | 0.189 | 37.8 |
| 2 | None | ½ | 0.0261 | 0.311 | 62.2 |
| 3 | None | 1 | 0.0293 | 0.351 | 70.2 |
| 4 | None | 2 | 0.0392 | 0.470 | 94.0 |
| 5 | None | 8 | 0.0420 | 0.504 | 100.8 |
| 6 | 5.0 | ¼ | 0.0120 | 0.144 | 28.8 |
| 7 | 5.0 | ½ | 0.0169 | 0.203 | 40.6 |
| 8 | 5.0 | 1 | 0.0228 | 0.274 | 54.8 |
| 9 | 5.0 | 2 | 0.0348 | 0.417 | 83.4 |
| 10 | 5.0 | 8 | 0.0380 | 0.457 | 91.4 |
| 11 | 5.0 | 16 | 0.0408 | 0.490 | 98.0 |
| 12 | 5.0 | 24 | 0.0420 | 0.504 | 100.8 |

Zinc dust is readily dissolved in cyanide solution. If there is an excess of zinc dust above that necessary to precipitate the dissolved metals, or if several hours are required for precipitation, as is the case if zinc dust is used to precipitate copper, an appreciable amount of zinc will be directly dissolved in the cyanide solution. The dissolution of the zinc is increased by increasing the period of agitation. The rate of dissolution slightly decreases in the presence of excess lime. Other experiments using the same quantity of cyanide in stronger solution show about the same rate of dissolution.

*Zinc Minerals Lower Extraction in Cyanidation of Precious-metal Ores*

The effect of each of three zinc minerals in cyanidation was determined by adding a weighed portion of the pure mineral to a precious-metal ore which, in the absence of zinc, gave good extraction by cyanidation. Details covering these experiments are given in Table 11.

The best extraction of precious metals is shown in the treatment of clean ore with fresh cyanide solution. The addition of cyanide-soluble zinc minerals lowers the extraction. The re-use of solutions gives erratic extractions corresponding with the zinc retained in the solutions. The amount of zinc in the pregnant solution coming from the ore gives a

TABLE 11.—*Effect of Soluble Zinc Minerals on Extraction of Gold and Silver by Cyanide*

Strength of original solution, 4.76 lb. free NaCN, 0.56 lb. CaO. Ratio of solution to ore, 5:1. Treatment, 24 hr. at 45° C.

| Sample Number | Zinc Mineral Added | Cycle Number | Solution Titrations, Pounds per Ton | | | | | | Zinc in Solution, Per Cent. | | Assays | | | | | | Extraction, Per Cent. | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | On | | | Off | | | | | Heads | | | Tailing | | | | | | |
| | | | Free NaCN | Total NaCN | CaO | Free NaCN | Total NaCN | CaO | On | Off | Ag, Ounces per Ton | Au, Ounces per Ton | Zn, Per Cent. | Ag, Ounces per Ton | Au, Ounces per Ton | Zn, Per Cent. | Ag | Au | Zn | |
| 1 | None | | 4.76 | 4.76 | 0.56 | 4.20 | 4.20 | 1.70 | None | None | 10.50 | 0.65 | None | 0.99 | 0.015 | None | 90.5 | 97.6 | None | Used a clean cyanide solution on ore containing no zinc. |
| 2 | Hydrozincite | 1 | 4.76 | 4.76 | 0.56 | 2.60 | 4.20 | 1.20 | None | 0.0776 | 10.49 | 0.66 | 1.28 | 1.31 | 0.090 | 0.87 | 87.5 | 86.4 | 32.00 | Fresh NaCN added to solution before re-use in cycle 2. |
| | | 2 | 3.65 | 5.20 | 1.20 | 2.60 | 4.75 | 0.60 | 0.0776 | 0.1016 | 10.49 | 0.66 | 1.28 | 3.00 | 0.215 | 1.16 | 71.5 | 67.4 | 9.35 | Solution treated with zinc dust at end of this cycle. |
| | | 3 | 2.40 | 4.75 | 0.70 | 2.60 | 4.40 | 1.10 | 0.1157 | 0.0842 | 10.49 | 0.66 | 1.28 | 1.32 | 0.085 | 1.36 | 87.5 | 87.1 | −6.25 | Negative zinc extraction, due to precipitation of zinc from solution. |
| | | 4 | 2.60 | 4.40 | 1.10 | 2.60 | 4.00 | 1.70 | 0.0842 | | 10.49 | 0.66 | 1.28 | 1.44 | 0.160 | 1.24 | 86.3 | 75.8 | 3.12 | Solution treated with zinc dust at end of this cycle. |
| | | 5 | 2.30 | 4.00 | 0.70 | 2.40 | 3.50 | 1.60 | 0.0950 | 0.0725 | 10.49 | 0.66 | 1.28 | 1.29 | 0.065 | 1.25 | 87.8 | 90.2 | 2.35 | |
| 3 | Zincite | 1 | 4.76 | 4.76 | 0.56 | 2.90 | 4.40 | 2.00 | None | 0.0852 | 10.45 | 0.60 | 1.22 | 1.36 | 0.035 | 0.76 | 87.0 | 94.1 | 37.70 | Same as cycle 1 above. |
| | | 2 | 3.90 | 5.35 | 2.00 | 2.95 | 4.90 | 1.90 | 0.0852 | 0.1152 | 10.45 | 0.60 | 1.22 | 1.52 | 0.085 | 1.09 | 85.4 | 85.9 | 10.65 | Same as cycle 2 above. |
| | | 3 | 2.65 | 4.90 | 1.60 | 3.00 | 4.50 | 1.70 | 0.1292 | 0.0852 | 10.45 | 0.60 | 1.22 | 1.46 | 0.045 | 1.28 | 86.0 | 92.5 | −4.90 | Same as cycle 3 above. |
| | | 4 | 3.00 | 4.50 | 1.70 | 2.90 | 4.05 | 2.00 | 0.0852 | | 10.45 | 0.60 | 1.22 | 1.56 | 0.090 | 1.13 | 85.0 | 85.0 | 7.40 | Same as cycle 4 above. |
| | | 5 | 2.60 | 4.05 | 0.90 | 2.80 | 3.65 | 2.00 | 0.0935 | 0.0730 | 10.45 | 0.60 | 1.22 | 1.41 | 0.035 | 1.11 | 86.5 | 94.1 | 8.60 | |
| 4 | Smithsonite | 1 | 4.76 | 4.76 | 0.56 | 3.10 | 4.40 | 1.70 | None | 0.0733 | 10.45 | 0.60 | 1.25 | 1.61 | 0.040 | 0.74 | 84.5 | 93.3 | 40.80 | Same as cycle 1 above. |
| | | 2 | 4.00 | 5.30 | 1.70 | 3.00 | 4.95 | 1.60 | 0.0733 | 0.1113 | 10.45 | 0.60 | 1.25 | 3.94 | 0.215 | 1.06 | 62.3 | 64.1 | 15.2 | Same as cycle 2 above. |
| | | 3 | 2.50 | 4.95 | 1.40 | 2.80 | 4.55 | 1.40 | 0.1250 | 0.0859 | 10.45 | 0.60 | 1.25 | 2.57 | 0.080 | 1.27 | 75.5 | 86.6 | −1.60 | Same as cycle 3 above. |
| | | 4 | 2.80 | 4.55 | 1.40 | 2.80 | 4.15 | 1.60 | 0.0859 | | 10.45 | 0.60 | 1.25 | 3.90 | 0.200 | 1.11 | 62.7 | 66.7 | 11.20 | Same as cycle 4 above. |
| | | 5 | 2.40 | 4.15 | 0.60 | 2.60 | 3.90 | 1.60 | 0.0930 | 0.0730 | 10.45 | 0.60 | 1.25 | 2.88 | 0.075 | 1.14 | 73.5 | 87.5 | 8.60 | |
| 1 | None | | 2.65 | 2.65 | 0.4 | 2.15 | 2.15 | 1.15 | None | None | 10.50 | 0.65 | None | 0.93 | 0.02 | None | 91.1 | 96.9 | None | Used a clean cyanide solution on ore containing no zinc. |

truer indication of the effect on extraction than the amount of zinc in the solution used to pulp the ore. This is explained by the fact that some of the zinc is precipitated out of solution during the agitation with fresh ore and lime. The erratic variation of zinc in the tailings from the different cycles is due to this precipitation of zinc from the solution. The higher the zinc content of the pregnant solution, the lower the gold and silver extraction in that particular cycle. In addition to the zinc entering solution by replacement of the precipitated metals there is a slight increase in the zinc content of the solution during the precipitation period, due to dissolution of zinc dust.

### *Zinc in Cyanide Solution Affects Gold and Silver Extraction*

The amount of zinc retained in the mill cyanide solution proportionally affects its efficacy as a solvent for precious metals from ore. Decreased extraction is noticeable when the solution contains 0.10 per cent. zinc. When it contains 0.36 per cent., the cyanide extraction of both gold and silver drops nearly 10 per cent. More details are given in Table 12.

A fresh solution containing no zinc gives maximum extraction of the precious metals. Extraction decreases in proportion to the increase of zinc retained in the cyanide solution. Experiment 5 of Table 12 shows that the free cyanide, as determined by silver nitrate titration, checks with the total cyanide titration. This indicates that the excess of caustic soda reacts to change the double sodium-zinc cyanide and produces a free cyanide titration equal to the total cyanide. However, it does not precipitate the zinc from solution. It appears, then, that merely changing the double sodium-zinc cyanide through reaction with caustic does not satisfactorily improve the condition for the cyanide dissolution of precious metals. The zinc must be removed from the cyanide solution to obtain maximum extraction.

In Table 12, the titrations show that although the free cyanide varies there is more than sufficient free cyanide at all times in each test to give, in clean solution, the maximum extraction of the precious metals.

Additional experiments show that the deleterious effect of zinc in a particular cyanide solution may be entirely overcome by the addition of more cyanide. In the usual plant practice this would result in excessive cyanide loss.

### *Double Sodium-zinc Cyanide*

It is generally considered that double sodium-zinc cyanide solution is a weak solvent for precious metals from their ores. Our experiments affirm this, and indicate that the solvent action is due to free cyanide liberated from the double salt. This liberation apparently occurs slowly on contact of the solution with a fresh ore charge; different ores release

TABLE 12.—*Experiments with Mixture of West End and Ramsey Comstock Ores*

Ratio of solution to ore, 3:1. Treatment, 24 hr. at 45° C. Heads assayed 10.89 oz. Ag, 0.56 oz. Au.

| Test Number | Solution Number | Solution Titrations, Pounds per Ton | | | | | | Zinc in Solution, Per Cent. | Tailing Assay, Ounces per Ton | | Extraction, Per Cent. | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | On | | | Off | | | | | | | | |
| | | Free NaCN | Total NaCN | CaO | Free NaCN | Total NaCN | CaO | | Ag | Au | Ag | Au | |
| 1 | 1 | 7.0 | 7.0 | 2.5 | 6.1 | 6.1 | 2.0 | None | 0.82 | 0.015 | 92.5 | 97.3 | No zinc in solution. |
| 2 | 2 | 6.1 | 7.5 | 2.2 | 5.8 | 6.5 | 2.4 | 0.104 | 0.98 | 0.015 | 91.0 | 97.3 | Zinc dust dissolved in fresh cyanide solution to obtain desired percentage of zinc in solution. |
| 3 | 3 | 5.4 | 7.6 | 2.5 | 5.0 | 6.6 | 2.6 | 0.163 | 1.00 | 0.015 | 90.7 | 97.3 | Same as No. 2. |
| 4 | 4 | 4.3 | 7.1 | 2.6 | 4.1 | 6.3 | 2.8 | 0.200 | 1.17 | 0.030 | 89.2 | 94.7 | Same as No. 2. |
| 5 | 5 | 7.7 | 7.7 | 13.1[a] | 6.9 | 6.9 | 11.3[a] | 0.360 | 1.67 | 0.060 | 84.7 | 89.3 | Zinc in solution as result of precipitating copper with zinc dust. |
| 6 | 6 | 2.65 | 2.65 | 0.4 | 1.85 | 1.85 | 1.50 | None | 0.93 | 0.02 | 91.5 | 96.5 | No zinc in solution. |

[a] NaOH used as the alkali and computed as CaO.

varying small amounts of free cyanide. Strong alkali reacts to change the form of combination of all the double cyanide. However, the zinc still remaining in the solution adversely affects its dissolving power. Table 13 shows the dissolving effect of sodium-zinc cyanide under varied conditions.

Maximum extraction is obtained with clean cyanide solution. On comparing experiment 3 with experiments 4 to 7 inclusive, it is plain that sodium-zinc cyanide furnished part of the cyanide used in the last-named tests. Lime readily frees some cyanide and strong caustic completely frees it, but both give practically the same dissolution of precious metals. This is explained by our former experiments, in that nearly all of the zinc in both cases is still retained in the cyanide solution and equally affects the dissolving power.

### *Removal of Zinc from Mill Solution*

The accumulations of zinc in mill solutions from any cause should receive prompt attention. The loss of precious metals from this cause is likely to be gradual and often overlooked because the loss is uniform and low. In the usual cyanidation with zinc dust as the precipitant the accumulation of zinc is slow and is often counterbalanced by precipitation through contact with fresh ore and lime together with the continual removal of waste solution with the tailings.

If the ore contains soluble zinc minerals or soluble copper minerals, and this copper is precipitated with zinc dust, the accumulation of zinc in the mill solution is fairly rapid and plainly shows by lowered extraction of the precious metals. Experiments on methods for the removal of zinc from cyanide solution are given in Table 14.

Lime, when added to a cyanide solution, liberates about 40 per cent. of the cyanide combined with zinc but removes by precipitation only a small amount of the zinc. In alkaline solutions a soluble sulfide is a more effective precipitant. The reaction is more active in warm solutions.

If the solution is acidified and the required amount of sodium sulfide added the zinc is almost completely precipitated. The acid method is practicable only when provision is made for safely retaining the liberated hydrocyanic acid and for its regeneration into an alkaline cyanide.

The mill solution regains the original dissolving efficacy for precious metals after the removal of zinc.

## Conclusions

1. All of the common copper minerals, excepting chrysocolla and chalcopyrite, are sufficiently soluble in cyanide solution under the usual conditions for cyanidation to cause excessive cyanide loss unless the cyanide that combines with the copper is regenerated.

TABLE 13.—*Dissolving Effect of Sodium-zinc Cyanide*

Heads assayed 10.50 oz. Ag, 0.65 oz. Au. Original sodium-zinc cyanide solution contained 0.168 per cent. Zn and 0.24 lb. of free cyanide. Ratio of solution to ore, 3:1. Treatment, 24 hr. at 45° C., except where otherwise noted in remarks

| Experiment Number | Solution Titrations, Pounds per Ton | | | | | | Tailing Assay, Ounces per Ton | | Extraction, Per Cent. | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | On | | | Off | | | | | | | |
| | Free NaCN | Total NaCN | CaO | Free NaCN | Total NaCN | CaO | Ag | Au | Ag | Au | |
| 1 | 7.0 | 7.0 | 2.5 | 6.10 | 6.10 | 2.0 | 0.99 | 0.015 | 90.5 | 97.6 | Used a strong solution of sodium cyanide. No sodium-zinc cyanide present. |
| 2 | 2.65 | 2.65 | 0.4 | 1.85 | 1.85 | 1.50 | 0.93 | 0.02 | 91.1 | 96.5 | Used a solution of medium strength. No sodium-zinc cyanide present. Heads to this test assayed 10.29 oz. Ag, 0.56 oz. Au. |
| 3 | 0.24 | 0.24 | 0.25 | None | None | 1.8 | 10.26 | 0.340 | 2.3 | 47.7 | Used a weak solution of sodium cyanide. No sodium-zinc cyanide present. Insufficient cyanide present. |
| 4 | 0.24 | 9.68 | None | 0.20 | 9.10 | None | 8.08 | 0.120 | 23.0 | 81.5 | Used original sodium-zinc cyanide solution. No lime or caustic added. |
| 5 | 0.20 | 9.10 | None | 0.24 | 8.10 | None | 8.15 | 0.100 | 22.4 | 84.5 | Re-used pregnant solution from test 4. No lime or caustic added. |
| 6 | 0.24 | 9.68 | None | 0.10 | 8.95 | None | 6.90 | 0.055 | 34.3 | 91.5 | Used original sodium-zinc cyanide solution. No lime or caustic. Time of treatment, 48 hr. |
| 7 | 0.24 | 9.68 | None | 0.10 | 8.90 | None | 5.81 | 0.035 | 44.7 | 94.6 | Used original sodium-zinc cyanide solution. No lime or caustic added. Time of treatment, 72 hr. |
| 8 | 0.24 | 9.68 | None | 4.60 | 8.70 | 0.60 | 1.48 | 0.025 | 86.0 | 96.1 | Used original sodium-zinc cyanide solution. Added 80 lb. lime per ton to ore before treatment. Treated pregnant solution with zinc dust. |
| 9 | 4.10 | 8.80 | 0.60 | 4.10 | 7.95 | 0.70 | 1.47 | 0.030 | 86.0 | 95.5 | Used barren solution from test 8. Add 50 lb. per ton to ore before treatment. Treated pregnant solution with zinc dust. |
| 10 | 3.85 | 8.00 | 0.70 | 3.80 | 7.35 | 1.20 | 1.48 | 0.025 | 86.0 | 96.1 | Used barren solution from test 9. Added 50 lb. lime per ton to ore before treatment. |
| 11 | 0.24 | 9.68 | None | 8.70 | 8.70 | 20.0[a] | 1.42 | 0.025 | 86.5 | 96.1 | Used original sodium-zinc cyanide solution. Added 100 lb. NaOH per ton to ore before treatment. |

[a] NaOH used as the alkali and computed as CaO.

2. The copper minerals containing arsenic or antimony will cause additional loss of cyanide and fouling of solution, due to dissolution of some of the arsenic and antimony.

3. The ratio, pounds of cyanide used to pounds of copper dissolved, varies from 1.85 to 2.75 for the different minerals. This variation is due to difference in the quantity of complex cyanide salts formed and the amount of cyanide used in dissolving other metals associated in the copper minerals.

4. The percentage of cyanide regenerated by the sodium sulfide-sulfuric acid method averages about 80 per cent. The regenerated solution is as active as a fresh solution in the dissolution of precious metals.

5. The amount of sodium sulfide used is directly proportional to the metals to be precipitated. The consumption of sulfuric acid varies as the strength of the pregnant solution in total cyanide (free and combined with metals), and lime or free alkali.

6. The presence of copper in a cyanide solution, in amounts not exceeding 10 lb. per ton, does not diminish the activity of the solution as a solvent for gold and silver, provided the solution contains free cyanide equal to the quantity needed in fresh solution to obtain maximum extraction.

7. The double sodium-copper cyanide solution in the absence of free cyanide is only a weak solvent for the precious metals.

8. The zinc minerals smithsonite, hydrozincite and zincite are sufficiently soluble under the usual conditions for cyanidation to cause rapid accumulation of zinc in solution and thus impair the efficacy of the solution as a solvent for precious metals.

9. Commercial zinc dust is also readily soluble in cyanide solution, therefore an excess over that necessary to precipitate the metals should be avoided. If zinc dust is used to precipitate copper from cyanide solution where the copper content accounts for excessive cyanide loss during the leaching period, the re-use of the cyanide solution will soon result in its becoming fouled with zinc.

10. The double sodium-zinc cyanide by itself is a weak solvent for gold and silver but the addition of lime or caustic liberates some free cyanide that will increase the efficacy of the solution. However, the zinc must be removed to obtain maximum dissolution of precious metals.

11. The experiments support the precipitation method (sodium sulfide and sulfuric acid) as a practical means of removing copper and zinc from cyanide solution and regenerating most of the combined cyanide in a form that is effective for the dissolution of the precious metals.

Our figures indicate that in most cases the cost of the chemicals will slightly exceed the selling price of the copper recovered. The merit of the process therefore depends on the value of the gold and silver associated with the copper mineral in the ores. It should be confined to

TABLE 14.—*Removal of Zinc from Cyanide Solution*

| Solution Number | Experiment Number | Method of Treatment | Solution Titrations,[a] Pounds per Ton: Before Treatment: Free NaCN | Before Treatment: Total NaCN | Before Treatment: CaO | After Treatment: Free NaCN | After Treatment: Total NaCN | After Treatment: CaO | Zinc in Solution, Per Cent.: Before Treatment | Zinc in Solution, Per Cent.: After Treatment | Zinc Precipitated, Per Cent. | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | Warm to 45° C. Add excess lime and agitate in stoppered bottle for 2 hr.; then filter. | 6.8 | 13.3 | None | 9.6 | 13.3 | 2.0 | 0.153 | 0.139 | 9.2 | Solution kept warm during agitation. |
| | 2 | Warm to 45° C. Make alkaline with lime. Then add theoretical amount of $Na_2S$ required to precipitate all the zinc. Agitate 5 min. and filter. | 6.8 | 13.3 | None | 11.0 | 13.3 | 1.5 | 0.153 | 0.120 | 21.6 | Soluble sulfides left in solution. |
| 1 | 3 | Solution at 23° C. Add excess of caustic soda and then $Na_2S$ as in experiment 2. Agitate 5 min. and filter. | 6.8 | 13.3 | None | 13.3 | 13.3 | 10.0 | 0.153 | 0.076 | 50.0 | Soluble sulfides left in solution. |
| | 4 | Heat to 65° C. Make alkaline with caustic soda. Add sufficient $Na_2S$ to precipitate 50 per cent. of the zinc. Agitate 5 min. and filter. | 6.8 | 13.3 | None | 13.0 | 13.3 | 5.5 | 0.153 | 0.091 | 40.5 | Small amount of soluble sulfides left in solution. |
| | 5 | Solution at 23° C. Add sufficient $Na_2S$ to precipitate 90 per cent. of the zinc. Acidify with $H_2SO_4$. Agitate 5 min. and filter. Agitation and filtration in open apparatus. | 6.8 | 13.3 | None | 2.0 | 3.5 | Sol'n acid | 0.153 | 0.045 | 70.5 | Only trace of sulfides left in solution. Loss of cyanide due to escape of HCN gas. |
| 2 | 6 | Solution at 23° C. Add sufficient $Na_2S$ to precipitate 50 per cent. of the zinc. Acidify with $H_2SO_4$. Agitate 5 min. and filter. Make filtrate alkaline with lime. Agitation and filtration in closed apparatus. | 2.8 | 5.85 | 0.6 | 4.1 | 5.8 | 1.5 | 0.137 | 0.070 | 49.0 | No soluble sulfides left in solution. |
| 3 | 7 | Solution at 23° C. Add sufficient $Na_2S$ to precipitate all zinc, copper and silver, then treat exactly as in test 6. | 2.4 | 4.0 | 2.5 | 5.5 | 5.7 | 1.8 | 0.0825 | 0.0109 | 86.8 | No soluble sulfides left in solution. |

[a] Any soluble sulfides in solution were precipitated with lead acetate and removed by filtration before titrating with silver nitrate.

precious-metal ore in which the copper is under a smelting grade; that is, ore in which the copper will not pay for a treatment method for its recovery, and its association with precious metals increases the usual cyanidation cost.

## DISCUSSION

J. E. Clennell, London, England (written discussion).—This paper interested me greatly, as I was associated with Mr. Leaver in metallurgical researches connected with the cyanide process some 30 years ago and am thoroughly familiar with the careful and painstaking nature of his work, and because I had at one time (more than 10 years ago) occasion to investigate one of the materials referred to in the paper; *viz.*, the Douglas tailings from Dayton, Nev. Unfortunately, I have now no record of the results obtained, but my impression is that the copper was largely soluble in cyanide and could readily be precipitated, with regeneration of most of the cyanide by means of zinc dust, especially in hot solutions.

As the use of zinc appears to be necessary in any case for recovery of the larger part of the gold, the advantage of the proposed process is not obvious to me. The more natural proceeding would seem to be to precipitate the gold, together with most of the copper and silver, by means of zinc, and to use sodium sulfide, in alkaline solution, from time to time for precipitation of the zinc (and incidentally a little of the silver) whenever the accumulation of zinc would otherwise reduce the solvent efficiency of the solution. The cyanide combined with zinc would thus be recovered as an effective solvent without the necessity of using acid, or a special enclosed apparatus such as is required by the authors' process. It is possible that the authors have already tried the method I have outlined; if so, it would be interesting to know why it was not adopted, and why they consider that their suggested method is preferable.

I should like to congratulate the authors on the presentation of a paper containing so many interesting and valuable data.

J. A. Carpenter, Reno, Nev. (written discussion).—This paper is of value not only for its experimental work on the suggested method of precipitating copper from cyanide solutions but also for its painstaking and detailed tests, which confirm or disprove statements scattered through the literature of cyaniding as to the action of cyanide solutions on copper and zinc minerals and their effect as double cyanide salts upon extraction results.

This paper would have been useful to me 15 years ago when I was experimenting to find the best way to cyanide "sweepings" from the tailing ponds at Tonopah. These "sweepings" contained the evaporated salts from waste mill solutions, and therefore had a high content of copper, zinc and reducing salts.

In my unsuccessful attempt to treat them by acid precipitation of the solutions I encountered serious trouble from the rapid increase in free cyanide and reducers, and in other impurities in the mill solutions; from the increasing amount of hydrocyanic gas inside and outside the plant, and from the sticky, slimy nature of the white precipitate. However, the final blow fell when the solution became so saturated with impurities that the silver precipitated out ahead of time on all iron surfaces of the agitators, pipe lines and filters. I still vividly remember my surprise in finding the inside of a centrifugal pump silver lined.

In the laboratory, this foul solution failed to precipitate its silver on zinc shavings but precipitated it on fresh iron turnings from the machine shop.

I suggest to the U. S. Bureau of Mines that it investigate the interesting chemistry of cyaniding "sweeps." These sweepings were later profitably treated at the Tonopah Belmont mill. Also the precipitation of copper and zinc from mill solutions

and the recovery of the hydrocyanic acid in fresh solution was later practiced at the Tonopah Extension mill.

This sulfide-acid precipitation method looks promising but there is need to follow it up with experimental work to find if possible a simple and inexpensive way to extract the silver from the sulfide precipitate at the cyanide plant, as there is too great a marketing loss in shipping the silver out as a combined silver and copper precipitate. May there be any condition in the precipitation as to time, temperature or addition of the sodium sulfide that might give a precipitation of one metal ahead of the other?

Also, if the same solution is to be used over again by adding alkali, then a present-day comparison with precipitation with aluminum dust, giving no double zinc cyanide as an impurity, would be most interesting.

The impression given by the paper is that even when high alkali is used to break the double zinc cyanide the zinc stays in solution and lowers the extraction. In practice sulfide ores should furnish, indirectly, sufficient sodium sulfide to precipitate out the zinc to a low content in the solution. If the ore contains marcasite, I well know there will be an excess of soluble sulfide, with the zinc in solution serving a useful purpose.

Why in experiment 3, Table 14, does the precipitating out of the zinc stop when the zinc in solution drops to 0.091 per cent.? Since sphalerite is somewhat soluble in free cyanide, does the freshly precipitated zinc sulfide tend to go back into solution?

From a long series of tests I once made on a silver chloride ore carrying oxidized lead and zinc minerals, I came to the conclusion that the double zinc cyanide was a good solvent for silver chloride. I would be interested in a test made on the pure mineral.

I would suggest that in recording tests the conditions as to the vigor of agitation and amount of aeration should be given, and also titrations on the reducing power of the solutions. In using a solution over again it is more often the reducers in the solution that lower the extraction than the double cyanide of zinc.

It would be interesting to hear from the operators at the Tonopah Extension and at Pachuca upon these points.

E. S. Leaver and J. A. Woolf (written discussion).—Answering Mr. Clennell: Our experiments show that in the precipitation of gold, copper and silver from cyanide solution by the use of zinc dust two serious difficulties were encountered:

1. Cyanidation of ores containing even 0.1 per cent. cyanide-soluble copper would in each cycle introduce sufficient zinc to lower the precious-metal extraction in the subsequent cycle unless the zinc were removed at the end of each cycle or excessive amounts of cyanide added to the mill solution. Zinc slowly precipitates copper from cyanide solutions. The best condition, 3 mol. of free cyanide for each mol. of dissolved copper, requires several hours for nearly complete precipitation even in warm solution. This means that a considerable quantity of the zinc dust would be directly dissolved during the precipitation period.

2. The equilibrium conditions with the use of sodium sulfide for the precipitation of zinc in cyanide solution are such that all the sodium sulfide does not react with the zinc, as part of the precipitate zinc sulfide redissolves in the alkaline solution; that is, soluble sulfide remains in the cyanide solution and would readily build up sufficiently to foul mill solutions. This is not the case in our proposed method of precipitation from acid solutions.

In reply to Professor Carpenter's questions: In the proposed process, silver and copper may be precipitated separately if desired. Sodium sulfide is an efficient precipitant for silver from alkaline cyanide solutions. Also, under this condition no copper is precipitated provided the solutions contain free cyanide. After the precipitation of the silver, if the solutions are made acid all of the copper is precip-

itated on the further addition of sodium sulfide. The silver product could be converted into bullion by the Nipissing, Canada, method; the copper sulfide, by low-temperature roast before melting.

It is known that sulfide ores tend to precipitate part of the zinc from the usual mill solution. In the cyanide treatment of ores containing even 0.1 per cent. soluble copper when zinc dust is used as the precipitant the rapid accumulation of zinc in the mill solution would foul the solution beyond the control of any soluble sulfide because of incomplete precipitation in alkaline solution.

Sodium sulfide is not a practical precipitant for zinc from alkaline cyanide solution. This is explained in section 2 of our reply to Mr. Clennell. It explains why in experiment 3, Table 14, a certain percentage of the zinc remains in the solution.

Experiments not included in this paper show that the double zinc cyanide is a fairly good solvent for silver chloride, or, in fact, any of the haloid silver minerals, as well as for gold; but even for these readily soluble minerals it is not as good a solvent as free cyanide. In most silver ores the silver content does not occur entirely as one of the haloid minerals, therefore the double zinc cyanide should be considered only as a weak solvent.

Titrations of many of the solutions for sulfocyanides and sulfides, two of the most ecmmon compounds that exercise a reducing influence, show that these compounds wore not present in sufficient amounts to affect the extracting power of the solution. The double cyanide of zinc accounted for the lower extractions.

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